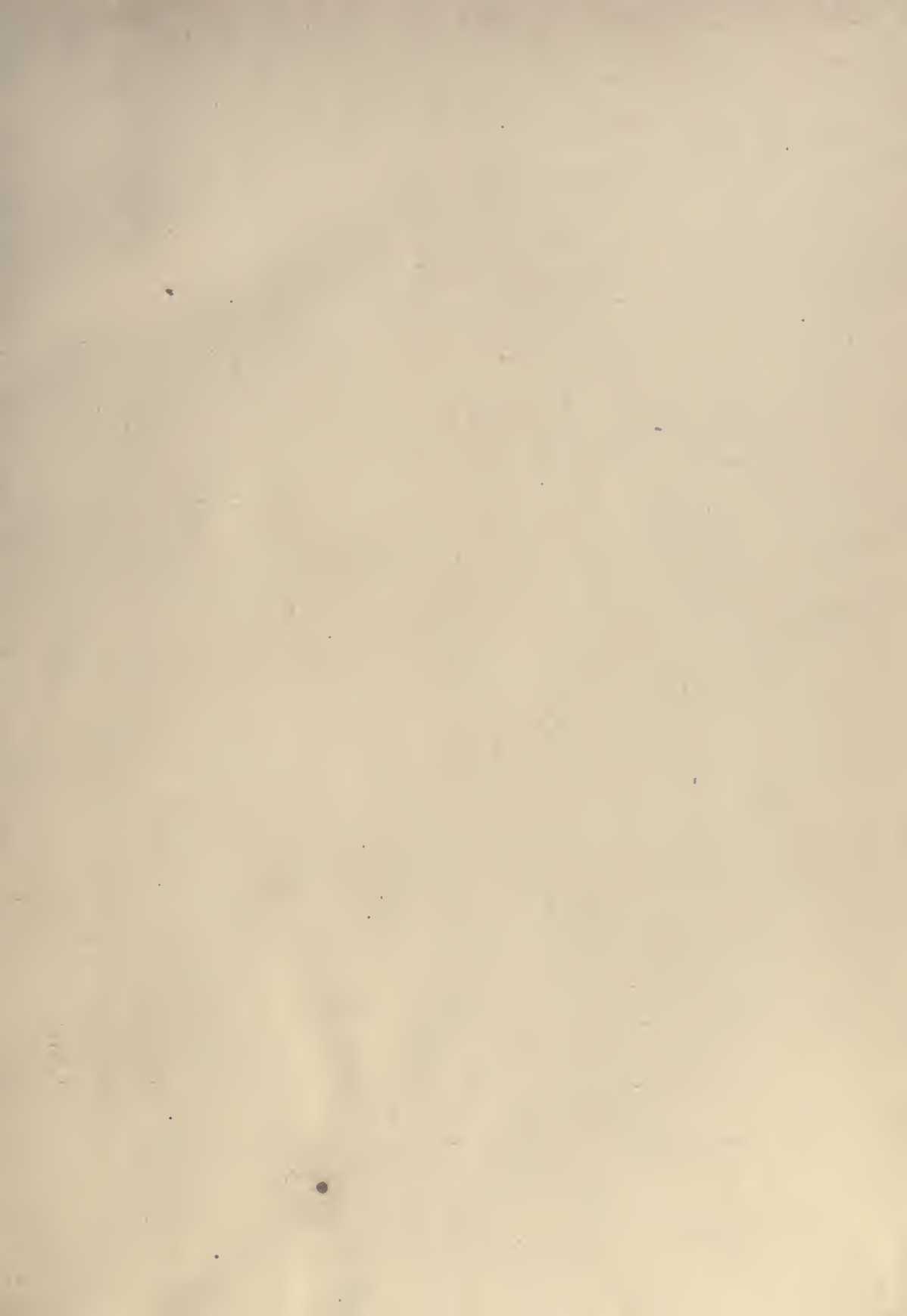
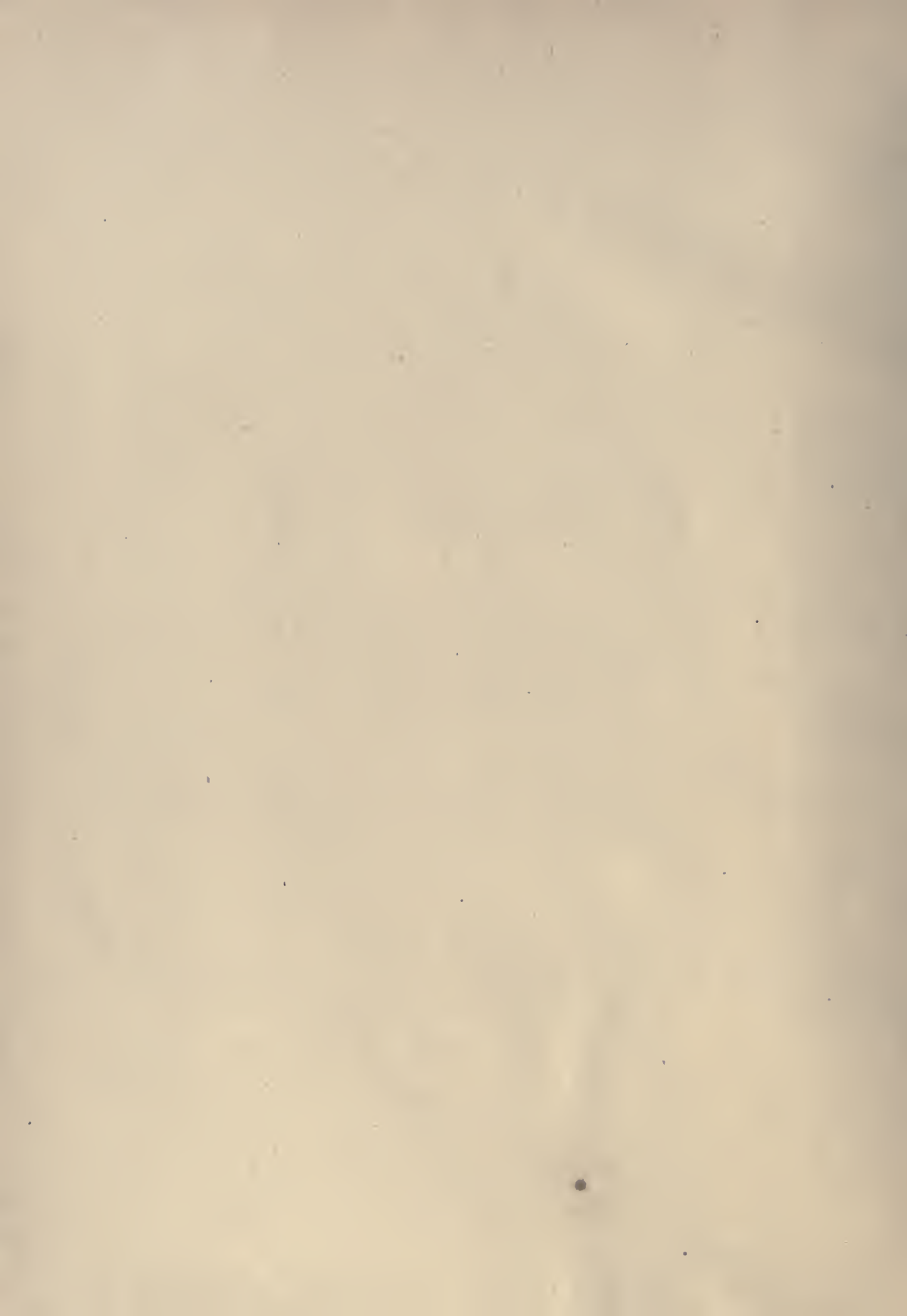








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THE CHEMICAL NEWS, JULY 30, 1909

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THE

CHEMICAL NEWS

AND

JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

SIR WILLIAM CROOKES, D.Sc., F.R.S., &c.

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VOLUME XCIX.

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No. 2562.—JANUARY 1, 1909.

TANTALUM, NIOBIUM, AND TITANIUM : OBSERVATIONS ON.*

PART II.—ON THE OPENING-UP OF MINERALS CONTAINING THESE BODIES.

By W. B. GILES, F.I.C.

FROM the time of the discovery of niobium by Hatchett in 1801 and of tantalum by Ekeberg in 1802, several methods have been proposed for the extraction of these bodies from the minerals in which they are found. These methods classified are :—

1. Fusion with alkaline hydroxides : Ekeberg (Rose and others).
2. Fusion with potassium carbonate and borax (Wollaston).
3. Treating with hydrofluoric acid or fusing with potassium bifuoride (W. Gibbs, Lawrence Smith, and Marignac).
4. Treating finely powdered minerals mixed with carbon with chlorine at a red heat (Ste.-Claire Deville).
5. Heating minerals mixed with carbon in an electric furnace (Moissan).
6. Fusion with potassium bisulphate (Berzelius, Rose). Lawrence Smith and Rose also use sodium bisulphate and ammonium bisulphate.

A short review of these processes and their respective advantages and defects is appended :—

METHOD NO. 1.—With regard to this process, Rose states that it would probably be preferable to any other if it did not require the use of silver crucibles, which are rather strongly attacked by caustic alkalis in a fused state. Another disadvantage is that only a very moderate heat can be used with silver vessels, and consequently there are produced acid salts *insoluble* in water which have to be fused again with fresh alkali to render them soluble. I have made many experiments on these lines with columbites, tantalites, and similar minerals, using, instead of the silver vessels, platinum crucibles lined on the interior with pure gold. With these crucibles higher temperatures can be obtained, but still the results are unsatisfactory. The fused alkali climbs the sides of the crucible very persistently and volatilises in white clouds, much insoluble acid salts are formed, and if manganese is present the gold crucible is attacked and gold is found in the solutions subsequently obtained. Wrought iron crucibles were also tried, but the "climbing" of the fused materials was even worse than with the gold crucible, and extended sometimes

almost to the bottom of the outside of the crucibles, though these were only half-full at the start. The following quantitative experiment was made on 5 grms. of very finely powdered and pure Australian tantalite (sp. gr. 7.24), which was heated with successive charges of pure potassium hydrate containing 72.3 per cent of K_2O . After each fusion the mass was thoroughly extracted with water, the acids were precipitated from the alkaline solution with dilute sulphuric acid mixed with sulphurous acid, the whole boiled, and the acids filtered, washed, and then strongly ignited, with addition of ammonium carbonate, to a constant weight. The matter insoluble in water—oxides of iron, acid salts, &c.—was also heated with dilute sulphuric and sulphurous acid, filtered, washed and ignited, weighed, and then fused again with fresh caustic potash. (See Table I.). This table shows that, starting with 5 grms. tantalite and 10 grms. of potassium hydrate, a fusion lasting three hours and ending with a red heat, only rendered 1.895 grms. of the acids soluble in water out of a total of 4.134 grms., or less than one-half, and that after a second fusion of the residue with 6 grms. more alkali there still remained insoluble 0.84 gm. which contained tantalic and niobic equal to nearly 14 per cent of the total amount present, and that at least four successive fusions would be necessary to entirely decompose the mineral. The disadvantages of this mode of procedure are obvious, a very large amount of alkali is employed, and much time and manipulation is necessary. I shall show further on that these defects arise from the fact that it is impossible to raise the temperature of the caustic potash sufficiently high to cause the easy formation of tantalates and niobates *soluble in water*. In fact, the alkali distils away and "climbs" the crucibles before the requisite heat can be obtained. After many trials I abandoned this method with some reluctance, since, as Rose points out, the metallic acids thrown down from soluble tantalates and niobates by precipitation with acids are always much more pure than those obtained by fusion with potassium bisulphate and exhaustion with hot dilute sulphuric acid. It is curious, however, to note that these successive fusions appear to cause a fractionation of the tantalic and niobic acids. In this tantalite the tantalic acid is in relatively very large amount to the niobic acid. Judging from the colour of the ignited acids, it would seem that the first fraction is almost pure tantalic acid, the second fraction being of a slate-blue colour is indecisive, but the third fraction would seem to contain most of the niobic acid, as the white acid becomes of a bright yellow colour when ignited; on cooling it becomes white again. This method does not free the metallic acids from tin, tungsten, &c.

METHOD NO. 2.—*Fusing Minerals with a Mixture of Borax and Potassium Carbonate* (Wollaston).—I have not

* The first part of this Paper appeared in CHEMICAL NEWS, vol. xcv., p. 1 et seq.

TABLE I.

	Time taken.		Matter left after treating with acid.	Acids precipitated from alkaline solution.	Colour of acids on ignition.
	Hours.	Grms.	Grms.	Grms.	
First fusion . .	3	10	2.766	1.895	Acids remained white.
Second fusion . .	2	6	0.840	1.543	Acids have a slate-blue colour, hot or cold.
Third fusion . .	1	2	0.047	0.649	Acids bright yellow when hot, white on cooling.
Residue . .	—	—	—	(0.047)	Yellowish white.
Total . .	6	18	3.653	4.134 grms. = 82.68 per cent.	

tested this process, since the introduction of sodium salts into materials containing tantalic acid gives rise to very slightly soluble salts, and is consequently objectionable. The effect of the boric acid is uncertain, but from what is known of its behaviour with tungstic acid and similar bodies it may be supposed that it would probably form complex compounds, boro-tantalates, boro-niobates, &c. Therefore its employment in the present state of our knowledge on these points does not seem advisable.

METHOD No. 3.—*Treating with Hydrofluoric Acid or Fusing with Potassium Bifluoride* (L. Smith, W. Gibbs, and Marignac).—The action of hydrofluoric acid on the various tantalic, niobic, and titanic acid containing minerals appears to resemble its action on various silicates. It is well known that while some silicates are readily decomposed by this agent, others, such as zircon, andalusite, staurolite, &c., are but little affected by it. Lawrence Smith has shown ("Original Researches," p. 353) that samarskite, euxenite, and hatchettolite are readily and conveniently opened up by this reagent, and he points out that the rare earths are separated in a dense and granular form as insoluble fluorides, while the metallic acids go entirely into solution. But when he states that "there is no columbate which does not readily yield to this treatment," he is stating more than the facts warrant. I have tried this method on various columbites and tantalites, and have found that even when the pulverisation of the minerals was effected as he directs by levigation with alcohol, &c., the opening up of even 1 grm. of the mineral is a very tedious and lengthy operation. Some of the complex titano-niobates are but little attacked by hydrofluoric acid. Fusion with bifluoride of potassium has some advantages; its action is more powerful than that of aqueous hydrofluoric acid. When used in conjunction with potassium bisulphate it will decompose many minerals which are hardly attacked at all by hydrofluoric acid, such as cassiterite, corundum, rutile, &c. (Clark, CHEMICAL NEWS, xvi., 232). The objections to these processes are:—That all the first operations have to be entirely carried on in platinum; the solutions, if cold and acid or neutral, can often be dealt with in ebonite vessels, and on a larger scale I have found the use of the paper-pulp utensils found in commerce coated with a hard resistant varnish very convenient. However, neither ebonite or the other utensils are practicable with alkaline solutions, especially when these are hot. Again, while the utility of hydrofluoric acid and fluorides as powerful agents (which are in many cases indispensable) cannot be denied, they are not substances which recommend themselves for use in the laboratory if they can be replaced by other bodies. Apart from the facts that their employment renders the ordinary laboratory utensils unavailable, and the deterioration of all glass vessels in their neighbourhood, their toxic effects are worthy of consideration. A long experience on a large scale with these bodies convinces me that the greatest care is necessary in their use. The incautious inhalation of hydrofluoric acid, spilling it on the hands and nails, and the internal administration of only a few milligrammes of the soluble bifluorides is attended with serious consequences. When minerals have been attacked by fluorine compounds, bases such as iron, manganese, and tin pass into solution with the metallic acids, and are subsequently removed with difficulty. This is especially the case with

tin. Hydrofluoric acid and fluorides resemble oxalic acid in this respect, that they prevent the precipitation of tin by hydric sulphide. Hall and Smith's researches (*Proc. American Phil. Soc.*, xlii., 181, 187, 190) show how tin kept turning up in the tantalic and niobic acids prepared from the double potassium fluoride salts, though their solutions had been treated repeatedly with hydric sulphide.

METHOD No. 4.—This process for opening up tantalites, niobites, &c., was recommended by Ste.-Claire Deville. I have had no experience of it as applied to minerals. The extreme volume occupied by the sublimed chlorides of tantalum and niobium and their contamination with ferric chloride are mentioned by Joly. H. Rose employed combustion tubes 5 feet long and nearly an inch in diameter to obtain 12 to 15 grms. of the sublimed chlorides. It appears to be more adapted for the working up of the acids obtained in the usual way than for minerals. It offers one great advantage that it separates the tin, titanium, germanium, and silicon in the form of very volatile compounds (zirconium will, however, be found with the tantalum and niobium chlorides), and up to the present time this chlorine treatment appears to be the only really efficient process for separating titanium from tantalum and niobium.

METHOD No. 5.—*Heating the Minerals mixed with Carbon in an Electric Furnace*.—Moissan reduces the minerals to fine powder, mixes them with charcoal from sugar intimately with the aid of a little sugar syrup, calcines the mixture in a Perrot-furnace, and then agglomerates the mass by pressure. These masses are then heated in an electric furnace with a current of 1000 ampères at 50 volts pressure for seven to eight minutes. In this way Moissan states that the whole of the manganese and the greater part of the iron and silicon are volatilised. The product is a brittle metallic crystalline mass, which contains all the tantalum and niobium combined with carbon. The mass reduced to powder is attacked by a mixture of hydrofluoric and nitric acid, the iron is separated by ammonium sulphide, and the mixed tantalic, niobic, and possibly titanic acids are then separated by Marignac's method. Or alternatively he treats the fused mass broken up into coarse powder with dry chlorine gas at a red heat, as in Deville's process. Since few laboratories have at command electrical installations capable of giving a current of 1000 amperes at 50 volts pressure, it is obvious that this mode of procedure can have but a limited application. I have found that tantalite and columbite in small pieces can be fused by means of an oxyhydrogen blowpipe, using a block of gas retort carbon as a support, into brittle fused buttons. These buttons, however, were not readily attacked by the mixture of hydrofluoric and nitric acid, probably because they contain a considerable admixture of fused or semi-fused tantalic and niobic acids.

METHOD No. 6.—*Fusion with Bisulphates of Potassium (Sodium or Ammonium)*.—Of all the methods proposed for opening up these minerals, the employment of bisulphate (or more properly pyrosulphate) of potassium, first suggested by Berzelius, seems to be the one almost universally adopted, especially for tantalites and columbites. Still, no one who has had much experience with it will deny that in many respects it leaves much to be desired. The fumes evolved upon heating any amount of the salt are extremely irritating, and the operations must therefore be

conducted under a hood with a good draught. The minerals, especially in the case of tantalites, must be reduced to an *extremely fine powder* if anything like a fair opening up is to be obtained. Lawrence Smith, for instance, speaks of 1 grm. of columbite requiring ten to fifteen minutes constant trituration in a four-inch agate mortar. My own experience is that even when the division of the mineral is carried on to an extent inconvenient in ordinary laboratories a complete resolution of the mineral is rarely, if ever, attained at one operation. However long the fusion is continued, the acids obtained by extracting the melt with hot dilute sulphuric acid always contain basic matters, and especially iron and zirconia; even a second fusion in many cases by no means removes all these impurities. One must not be misled by the white appearance of the acids; they may be nearly white, and yet contain as much as 4 per cent of iron and other impurities. Adding a few drops of ammonium sulphide to the moist acids should not blacken them (lead or iron). The acids not ignited or strongly heated ought to be perfectly soluble in a hot solution containing their own weight of oxalic acid. Any insoluble matter indicates lime, lead, thorium, ceria, and yttria group of metals, &c. The quantity of saline matters introduced by the large amount of potassium bisulphate generally recommended is inconvenient when the basic matters have to be estimated, and as the bisulphate invariably loses a good deal of its sulphuric acid during the heating, there is a tendency to form in some cases extremely insoluble double sulphates, such as zirconium-potassium sulphate, which is, according to Fresenius, almost absolutely insoluble in water, and in hydrochloric acid *if precipitated hot*. Again, it has been shown, especially by Prior (*Mineralogical Mag.*, xv., 83), that when much titanic acid is present along with tantallic and niobic acids, "on fusion with acid sulphate of potassium and treatment of the melt with a 5 per cent solution of sulphuric acid, practically the whole passed into solution." I can quite confirm this statement from my own experience; it has long been known that this method, recommended in most text-books as a means of separating titanic acid from tantallic and niobic acids, was imperfect, but Mr. Prior has demonstrated that in the presence of large amounts of titanic acid it is absolutely untrustworthy and misleading, and consequently the published analyses of minerals containing these three acids require in some cases considerable corrections. These minerals contain very frequently as constituents other metals, such as tin, tungsten, lead, antimony, and germanium, and when such minerals are treated with alkali bisulphates, the tin and tungsten certainly, and the antimony and germanium probably, become so firmly united to the tantallic-niobic acids that their separation becomes a matter of extreme difficulty. Berzelius recommended that the washed tantallic-niobic acids should be digested with ammonium sulphide to remove the tin, tungsten, &c. Rose ("Chimie Analytique Quantitative," 1862, p. 456) found that this plan did not answer, and he recommended fusing the acids with six times their own weight (!) of a mixture of equal parts of dry sodium carbonate and sulphur. Why such an enormous excess of alkaline sulphide is used is not apparent. Rose states, however, that this fusion converts a good deal of the acids into insoluble sodium tantalates and niobates, and consequently the whole must be again fused with six times its weight of potassium bisulphate and treated with hot dilute sulphuric acid as before to free them from the combined soda. Rose says naively: "Ce traitement est un peu compliqué," but one fears that those chemists who have tried it would use stronger terms before they finished the operations. Dr. Edgar Smith says on this point:—"Our own experience leads us to say that the removal of tungsten and tin from columbium and tantalum oxides cannot be realised by digestion with ammonium sulphide. Indeed, not only did we find the fusion with the sodium carbonate and sulphur necessary, but that working on large quantities of material, as in our case, *two or even three refusions with these reagents were*

found necessary" (*Proc. Am. Phil. Soc.*, xlv., 157). Blomstrand also (*Fourn. Prakt. Chem.*, xciv., 40) did not obtain favourable results with this method. He points out that if a low temperature is applied in the fusion the tin, tungsten, &c., are not removed, while if a higher heat is employed the tantallic and niobic acids pass into solution along with the tin and tungsten sulphides when the melt is treated with water. It is therefore apparent that the complete removal of the tin, tungsten (and probably also of antimony and any germanium) is an exceedingly tedious operation when carried out in this manner. It seems to be commonly assumed that the residue left on treating with water or dilute sulphuric, the result of a fusion of a tantalate or niobate with potassium bisulphate, is tantallic or niobic acid mixed with a certain amount of basic matters. But, as a matter of fact, this residue is really a tantallic or niobic sulphate (Moissan, "Chimie Minérale," ii., 139). Hermann (*Fourn. Prakt. Chem.*, 1872, 12), v., 66) found in the product obtained by fusing tantallic acid with potassium bisulphate, exhausting the melt with boiling water, and drying at 100° C., 85.25 per cent of tantallic acid, 5.23 per cent of SO₃, and 9.52 per cent of water, corresponding fairly well with the formula 3(Ta₂O₅).SO₃.9H₂O. Rose points out that the acids can be washed continuously for several weeks without eliminating all the sulphuric acid. When the washed sulphides are collected on paper filters one observes that the paper becomes quite rotten, and even charred when dried at 100° C., from the liberation of sulphuric acid. It has been recommended that the acids should be washed with dilute ammonia in order to get rid of the sulphuric acid. I have tried this on the acids obtained from columbite by fusion with sodium pyrosulphate. After the acids had been well washed with dilute sulphuric acid and then with water only, they were stirred up with a slight excess of ammonia. This caused a great change in their appearance; at the beginning they were pulverulent, but the treatment with ammonia converted them into a flocculent state. Yet in this condition they filtered bright and fairly well. But the *clear filtrate contained a surprising amount of the acids*, which came down when the ammonia was just over-neutralised with hydrochloric acid. The precipitate was filtered off and washed. On examination it gave a very strong reaction for niobic acid with zinc dust, but only a very faint indication of titanic acid with peroxide of hydrogen; it was not examined for tantallic acid. It is clear that the acids (or rather the sulphates) are *distinctly soluble in ammoniacal ammonium sulphate*, and as this mode of procedure has been recommended in the quantitative analysis of the acids, a word of caution as to the error it involves is not out of place. It is not improbable that when the moist crude acids are treated with sulphide of ammonium in order to extract the tin, tungsten, iron, &c., that a certain amount of niobic and, perhaps, tantallic acid will be found to go into solution along with the tin and tungsten sulphides, as ammonium sulphate must be formed in this case also. I intend when time permits to follow up this question of the solubility of the acids in ammoniacal ammonium sulphate; possibly only niobic acid may thus be dissolved and not titanic or tantallic acid. The use of sodium pyrosulphate instead of the potassium salt seems advisable on the ground that it is far more soluble, and when rare earths are present it has not so much tendency to form insoluble double sulphates. It appears to me, however, to lose sulphuric acid at a lower temperature than the potassium salt. I have tried on some occasions ammonium bisulphate as recommended by Rose. I found that finely ground columbite can be opened up with this reagent, heating in Jena glass beakers, but tantalite seems but little attacked. I have never, however, been able to completely dissolve columbite in the fused salt so as to get a clear glassy mass which would dissolve in water temporarily to a clear fluid in the manner spoken of by Rose. There was always a residue which the most prolonged heating failed to dissolve. Vessels of fused silica are very

useful for these fusions with bisulphates, and are to be preferred to platinum, which metal is not unaffected by long heating with acid sulphates. Solutions of titanate hydrate in nitric and sulphuric acid seriously attack both platinum and platinum-iridium basins when they are evaporated in them. This is alluded to by Rose (*Chimie Analytique Qualitative*, p. 1028), but appears to have been overlooked since his time, as Fresenius recommends platinum dishes for the estimation of titanate acid in acid solutions ("Quantitative Analysis," p. 196). I have found that when pure titanate acid is fused with potassium or sodium carbonate, the melt dissolved in nitric acid, and the whole evaporated to dryness on the water-bath in platinum, on taking up with water and dilute nitric acid the insoluble titanate acid is quite grey in colour and the dish has lost in weight considerably. According to Rose, tantalate and niobate acids do not act in this way on platinum. I first noticed this action of titanate acid solutions on platinum in attempting to separate a mixture of a quantity of rare earth oxides from a considerable amount of titanate acid with which they were mixed, by dissolving in nitric acid and evaporating to dryness on the water-bath in a platinum basin, as one would proceed for the estimation of silica.

Requiring some quantities of pure tantalate, niobate, and titanate acids for various experiments, I was led to think whether it would not be possible to devise some better way of extracting these bodies from their native compounds, and especially from ordinary columbite and tantalites, so that as far as possible the use of fluorine compounds and the employment of platinum vessels should be avoided, and also that the very tedious means hitherto made use of for the separation of tin, antimony, iron, and other impurities could be improved. As my efforts in these directions have not proved unsuccessful, I offer the results of them to our readers. Desiring to obtain some materials uniform in composition so that experiments could be repeated under like conditions, I obtained some time ago parcels of minerals in some quantity. One of these was columbite; this I obtained from a dealer who had had it in stock for many years. It was marked "Columbite from Middleton, Connecticut, U.S.A." The weight of this was about 10 kilograms. It was externally very free from foreign matters, and many of the lumps were highly crystalline and beautifully iridescent. Another material was massive tantalite, partly from Greenbushes, West Australia, and partly from the Northern Territories, Australia. These were also fairly free from foreign admixtures; the exterior of some of the pieces, however, was covered with a thin drab-coloured adherent coating which could not be wholly removed by washing, and as it contained tantalate acid it appeared to consist of what is known as tantalate ochre. The weight of these tantalites was about 30 kilograms.

(To be continued).

LECTURE EXPERIMENTS SHOWING THE FORMATION OF THE NITRIDES OF BARIUM, STRONTIUM, CALCIUM, AND ALUMINIUM.

By H. RUSSELL ELLIS, B.Sc., F.C.S.

If a mixture of the oxide of one of the above metals and magnesium powder is spread over an iron sand-tray, and ignited by means of a match or a piece of burning magnesium, a reaction takes place similar to Goldschmidt's thermite reactions. The reaction is intense, but is not violent, no violent evolution of the products of the reaction occurring.

The mixtures were made:—

- | | |
|---------------|--|
| 1. BaO + Mg. | 5. CaO + Mg. |
| 2. BaO + 2Mg. | 6. CaO + 2Mg. |
| 3. SrO + Mg. | 7. Al ₂ O ₃ + 3Mg. |
| 4. SrO + 2Mg. | |

The magnesium powder replaces the other metals owing to the heat of combustion of magnesium being greater than that of barium, calcium, strontium, and aluminium (see *Trans. Far. Soc.*, iv., Part II., p. 130).

In order to commence this reaction, a high initial temperature is necessary, and this is supplied by the burning magnesium.

The free metal, as soon as it is produced, being in contact with air, immediately combines with oxygen and nitrogen.

With BaO, CaO, and SrO the product was quite yellow, and on moistening with water smelt very strongly of ammonia; with Al₂O₃ the product was black, but also smelt strongly of ammonia on adding water.

In the experiments with the oxides of the alkaline earths, carbonate, hydrate, and peroxide must be absent; if these are present the action is violent, and the formation of nitride is much decreased.

Calcium oxide, if the carbonate is present, gives no nitride, carbide, nor cyanide; barium and strontium oxides containing appreciable quantities of carbonates yield nitride, cyanide, carbide, and, possibly, cyanamide.

Excess of magnesium powder, as a rule, produces a larger yield of the nitride, possibly by union with the oxygen of the air leaving the nitrogen for the other metal.

Estimations of the amount of nitrogen gave the following:—

		Maximum yield.
1. BaO + Mg	Per cent of Ba ₃ N ₂ = 24.4	78.4
2. BaO + 2Mg	" " = 43.33	64.5
3. SrO + Mg	" Sr ₃ N ₂ = 33.69	70.6
4. SrO + 2Mg	" " = 53.84	54.6
5. CaO + Mg	" Ca ₃ N ₂ = 33.65	55
6. CaO + 2Mg	" " = 31.55	37.9
7. Al ₂ O ₃ + 3Mg	" Al ₄ N ₃ = 11.145	40.9

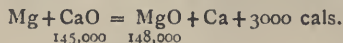
In the last column under the heading maximum yield is given the percentage of nitride that would be produced if the whole of the metal from the oxide became converted into the nitride, e.g., 3CaO + 6Mg + 3O + 2N = Ca₃N₂ + 6MgO.

The free metal after the reaction was always very small, never amounting to more than 3 per cent.

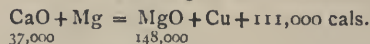
That the nitride does not consist of magnesium nitride is evident from the following considerations:—

When magnesium burns in air, either as the powder or the ribbon, less than 1 per cent of nitride is obtained, and when an oxide is reduced, the metal of which does not form a nitride, the yield of nitride is again less than 1 per cent.

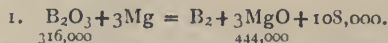
Magnesium nitride readily burns, and if a great heat evolution takes place the nitride would burn; now, when Mg reduces CaO the heat evolution is not excessive—



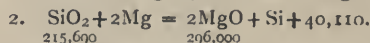
with such a reaction, as a large evolution of heat occurs:—



In the first case we might expect that any magnesium converted into the nitride would remain as such, but from the study of two other reactions in which a similar small heat evolution occurs, no nitride is produced. The two reactions in question are:—



(For one molecule of MgO 36,000 cal. being liberated).



(For every molecule of MgO 20,000 cal. being liberated).

Again, using excess of magnesium, although the yield of nitride is increased, the amount produced is never above that which could be produced from the metal obtained from the oxide. The above experiments are being repeated *in vacuo*, and in an atmosphere of nitrogen.

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COMBUSTION ANALYSIS.*

By JAMES WALKER, F.R.S., and THOMAS BLACKADDER,
B.Sc., University College, Dundee.

THE process of Dennstedt for the elementary analysis of organic compounds by combustion in oxygen with the help of platinised quartz was tried in this laboratory, and in expert hands was found to be both rapid and accurate. The average student, however, experienced great difficulty in the conduct of the combustion, and it occurred to us that the advantages of the apparatus of Dennstedt, so carefully worked out by him in detail, might be applied to the ordinary method of combustion by means of copper oxide.

If one inspects a tube in which a copper oxide combustion is being conducted, it is found that the oxide actually reduced to metallic copper after the combustion of the volatile matter is completed, rarely extends for more than an inch or two along the tube, unless the process has been accidentally "rushed." It seemed, therefore, possible to reduce the dimensions of the combustion-tube to such an extent as to secure the advantage of the Dennstedt furnace, which from its lightness of construction admits of rapid heating and cooling. This we discovered to be the case, and in reality there is no greater

while still hot to a tube A, Fig. 2, which is then closed with a stopper, through which passes a calcium-chloride tube to protect the copper oxide from atmospheric moisture. If the substance to be analysed is a solid, it is weighed off in a small stoppered bottle B, Fig. 2, the neck of which fits into the constriction of A, so that the substance may be mixed in B with a quantity of copper oxide from A, with as little exposure to the atmosphere as possible. The end of the combustion-tube fits into the wider part of A, so that it also may be conveniently charged with copper oxide from the ignited supply. After the combustion-tube has received its charge of copper oxide, the mixture of substance and copper oxide is transferred from B into the combustion-tube, the neck of the stoppered bottle being of such a diameter as to fit inside the end of the latter. The bottle is then "washed out" once or twice with copper oxide, received as before from A, and emptied into the combustion-tube. The absorption-tubes and oxygen supply are next attached and the combustion begun. The two burners at the front (absorption end) of the tube are lit and tiles are placed over them, the heat being as far as possible confined to the portion of the tube covered by the tiles by means of screens of asbestos paper. When the copper oxide has attained dull redness, the third Bunsen is lit at the other extremity of the tube without a tile. The heat from this Bunsen gradually volatilises the substance,

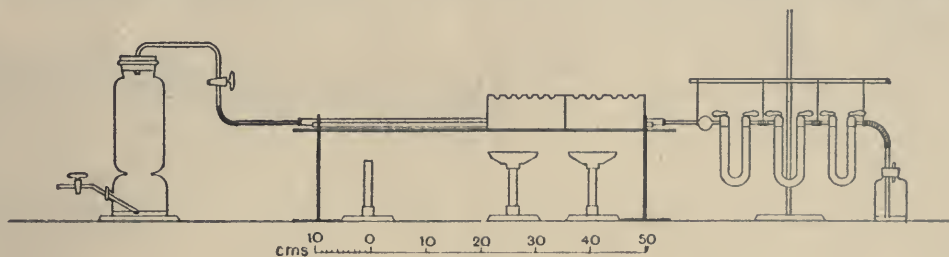


FIG. 1.

difficulty in performing a copper oxide combustion in a shortened Dennstedt furnace, heated by three Bunsen burners, than in a furnace of the customary type heated by thirty. The saving of initial outlay on the furnace, and on the current consumption of gas is, of course, comparatively great, but a still more considerable advantage is that the combustion may be done on the worker's bench without inconvenience to himself or to his neighbours.

The furnace employed by us, together with the burners, absorption-tubes, and the purifying apparatus for the supply of oxygen, are practically all as described by Dennstedt, and shown to scale in Fig. 1. The chief modification is that the furnace is cut down to 60 cm. in length. The combustion-tube is of Jena glass, 66 cm. long, and need not be more than 8 mm. internal diameter. The total volume of such a tube is only about 30 cc., and the charge of copper oxide, including spirals, weighs only 35 grms. Two of the burners are supplied with attachments for spreading the flame into a flat sheet; the third is used for local heating, but towards the end of the combustion, when the whole tube is heated, it also may be provided with a flame-spreader.

The copper oxide employed is coarsely powdered and sifted free from fine dust, which during the combustion might clog and stop the tube. The combustion is carried out in a current of oxygen, and the calcium chloride and soda lime absorption-tubes are always weighed filled with the same gas.

The method adopted for mixing the substance with copper oxide, and transferring it to the combustion-tube, is a slight modification of that used by Professor Thiele, of Munich. The copper oxide after ignition is transferred

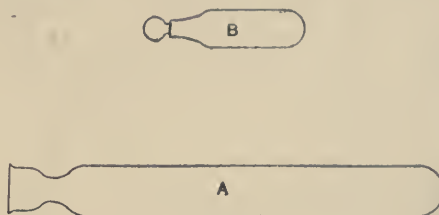


FIG. 2.

with or without decomposition, the volatile products being for the most part burned in the moderately rapid stream of oxygen (two to three bubbles per second) which is all the time passing through the apparatus. The Bunsen is gradually moved forward as the combustion proceeds, tiles being placed behind it to keep the tube still hot. Under ordinary conditions there is no visible reduction of copper oxide to metallic copper, although towards the end of the combustion the oxide usually gloves immediately behind the tiles at the absorption end of the tube. To burn any carbon that may be left on the tube by decomposition, all the tiles are placed in position, and the three burners adjusted so that the tube is heated as uniformly as possible to dull redness. The carbon at this temperature is not graphitised and burns off readily. When the oxygen comes freely through the indicator bottle at the end of the apparatus, the combustion is finished, and very little sweeping out is necessary, owing to the small volume of the apparatus. Immediately after the combustion, the copper oxide is returned to the tube A, and is ready for the next analysis.

The time occupied between attaching and removing the absorption-tubes need not exceed half an hour. The

* From the *Proceedings of the Royal Society of Edinburgh*, xxviii., Part ix., No. 44. We are indebted to the Royal Society of Edinburgh for the blocks illustrating this Paper.

amount of oxygen consumed in a combustion averages 800 cc.

In order that an idea may be formed of the rapidity and accuracy of the method, the following results may be quoted. Four combustions of succinic acid were performed, including weighing, between 9 a.m. and 1 p.m., two sets of absorption-tubes being used, in order that no time might be lost in waiting for the tubes to cool before weighing.

Quantity taken.	Percentage carbon.	Percentage hydrogen.
0.1866 gm.	40.61	5.28
0.1492 "	40.44	5.20
0.1890 "	40.48	5.18
0.1733 "	40.56	5.20

(The theoretical percentages for $C_4H_6O_4$ are carbon = 40.68, hydrogen = 5.09).

If the substance contains nitrogen, a metallic copper spiral 7 cm. long is, as usual, placed at the front of the tube, and the current of oxygen is passed at a slower rate at the beginning of the combustion. For acetanilide the following percentages were obtained:—Carbon, 71.03, 71.24; hydrogen, 6.72, 6.89, the numbers for the formula C_8H_9NO being 71.11 and 6.67 respectively.

When the substance is a liquid it is weighed off in a small bulb with a sealed capillary, the tip of the capillary being broken off before its introduction into the tube. The best results are got when the capillary is comparatively wide and about 8 cm. long. The open end of the capillary, surrounded by the copper oxide, faces the stream of oxygen. The liquid, when the copper oxide in the front of the tube has reached dull redness, is slowly distilled out of the bulb into the copper oxide at the cool end of the tube by means of a small Bunsen flame applied directly to the upper side of the tube over the bulb. The combustion is then continued as for a solid.

When a volatile liquid, such as benzene, is burned, it is introduced into the tube in a small sealed bulb terminating in a capillary at either end. The longer capillary (8 cm.) is plugged with fusible metal (compare Hempel, "Gas Analysis," p. 341), and the shorter (3 cm.) is sealed off in the flame after the bulb has received its charge of benzene. In this case it is advisable not to surround the bulb and capillaries with copper oxide, but to leave the whole clear at the back of the tube. The little plug of fusible metal at the end facing the current of oxygen is melted by the application of the flame above the combustion-tube, and the benzene is gradually vaporised by very gentle heating. The following result was obtained by this method:—

Carbon = 91.94 per cent; hydrogen = 7.83 per cent.
Calculated for C_6H_6 —Carbon = 92.31 per cent;
hydrogen = 7.69 per cent.

A combustion-tube of the same dimensions may be used for estimating nitrogen by the direct method. In this case a current of carbon dioxide is substituted for the current of oxygen, the nitrogen being collected over concentrated potash solution. The reduced copper spiral necessary in this case need not exceed 7 cm. in length. The percentage of nitrogen in aniline found by this method was in two experiments 15.09 and 15.25, the percentage required for the formula C_6H_7N being 15.05. Equally satisfactory results were obtained with acetanilide and hippuric acid.

To show that the method gives satisfactory results in the hands of a beginner, the following consecutive analyses may be quoted from the notebook of a student who had no previous experience of organic combustions:—

		Carbon.	Hydrogen.
Succinic acid.	Found I.	39.91	5.19
	" II.	40.54	5.20
	Calculated	40.68	5.09
Cane sugar.	Found I.	40.83	6.48
	" II.	41.81	6.63
	" III.	42.12	6.41
	Calculated	42.11	6.43

It is apparent, then, that the method as here described is well adapted to ordinary laboratory work, and compares very favourably with the copper oxide method as usually employed in respect of economy in apparatus, gas, and time, and of the greatly increased comfort of the operator.

ON THE DETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS.*

By C. W. BACON.

1. Introductory.

HALOGENS are at present determined in organic compounds almost exclusively by the method of Carius. While generally reliable, the method is quite laborious. First, it requires some hours of actual work, including as it does a gravimetric determination of silver halide. Besides, eight or nine hours heating with fuming nitric acid involves a delay in getting the final result, which is at times extremely inconvenient.

About two years ago Stepanoff (*Ber.*, 1906, xxxix., 405) published a method for the quantitative determination of halogens in organic compounds based on the reducing action of nascent hydrogen. He dissolves a weighed amount of the halogen compound in 20 to 40 cubic centimetres of 98 per cent alcohol in an Erlenmeyer flask connected with a reflux condenser, places the flask on a water-bath, and adds gradually through the condenser twenty-five times the amount of sodium corresponding to the reaction $R.Hlg + C_2H_5.OH + 2Na = Na.Hlg + C_2H_5.ONa + R.H$. When the reaction is over he adds 20 to 40 cubic centimetres of water, distils off the alcohol, acidifies strongly with nitric acid, and determines the halogen in the resulting solution by Volhard's method.

Stepanoff's method was tried in these Laboratories, exactly as described by the author, in connection with a study of the esterification of some refractory aromatic acids containing halogens. The results, however, were entirely unsatisfactory. The figures yielded by consecutive analyses of one and the same substance differed greatly from one another, and were many per cent removed from the truth.

At the request of Professor Rosanoff I then undertook to re-investigate the subject with a view to ascertaining under what conditions, if at all, nascent hydrogen can really be relied upon to reduce organic halogens quantitatively. The analytical conditions and procedure recommended below are the result of a large number of painstaking trials. If the simple directions are followed, success may be confidently expected in every case. A single determination requires about two hours; but if three or four determinations are carried on simultaneously a considerable number of analyses can be conveniently performed in the course of a working day.

2. Analytical Directions.

Introduce about 0.2 gm. of the halogen compound into a dry pear-shaped (Kjeldahl) flask.

If w is the number of grms. of the compound taken, add $156w$ cubic centimetres of alcohol (at least 98 per cent) if the compound contains chlorine, or $68w$ cubic centimetres if the compound contains bromine, or $44w$ cubic centimetres if the compound contains iodine. Connect the flask with a reflux condenser, clamp it over a square of wire gauze covered with a thin sheet of asbestos, and warm with a Bunsen burner until the substance is dissolved.

Introduce very gradually, through the condenser, a total of $19.5w$ grms. of sodium if the compound contains chlorine, or $8.5w$ grms. of sodium if the compound contains bromine, or $5.5w$ grms. of sodium if the compound contains iodine. (These quantities represent about fifteen times the amount

* Contributions from the Chemical Laboratories of Clark University.

of sodium corresponding to the chemical equation given in the preceding section, assuming the substance analysed to contain 100 per cent halogen). *This operation should be extended over at least thirty minutes.* Toward the end of the operation maintain the solution at the boiling-point by means of a Bunsen burner, and when the introduction of the sodium is complete boil the solution gently for one hour longer.

Then allow the temperature of the solution to fall to about 50° or 60°, dilute freely, through the condenser, with cold water, acidify with nitric acid, add a moderate excess of silver nitrate, and on complete cooling determine the excess of silver titrimetrically by Volhard's method. If the halogen involved is chlorine, filter out the precipitated silver halide before titrating with sulphocyanate. If the halogen is bromine or iodine, filtration is unnecessary (see Rosanoff and Hill, *Journ. Am. Chem. Soc.*, 1907, xxix., 269; *CHEMICAL NEWS*, xcvi., 299).

A few additional remarks may not be superfluous. The statement that the liquid should be boiled for an hour after the solution of the sodium is complete may seem surprising; for sodium ethylate is believed by some to have no action upon halogen compounds of the aromatic series. While the additional boiling is probably unnecessary in the case of aliphatic compounds, the following experiment will show that the operation is not useless in the case of refractory aromatic compounds. An alcoholic solution of hexachloro-benzene was boiled for one hour with the amount of sodium ethylate required by the above directions. The solution, diluted with water and acidified, was found to contain no less than 25 per cent of the amount of sodium chloride corresponding to the hexachloro-benzene used. While in similar experiments I was unable to transform monobromo-benzene into phenetol, there is no doubt but that the alcoholates of sodium attack halogens in a benzene ring quite vigorously. In fact, if the action were not somewhat too slow for analytical purposes, it might be employed, independently of any other method, for the quantitative estimation of halogens in organic compounds.

Special experiments showed that distilling off the alcohol (as Stepanoff does) before titrating with sulphocyanate is unnecessary. In the solution copiously diluted with water the alcohol has no effect upon the end-point.

Finally, Kahlbaum's sodium was found to be sufficiently pure for use in connection with the method here proposed.

3. Some Test Results.

The following results were obtained by the method proposed:—

1. A sample of 1-2-4-6-trichlorobenzoic acid prepared in this laboratory was found to contain 47.29 per cent of chlorine. The amount corresponding to the formula $C_7H_3O_2Cl_3$ is 47.19 per cent.
2. Two samples of ethyl 1-2-4-6-tribromobenzoate, containing theoretically 61.99 per cent of bromine, gave 61.32 per cent and 61.25 per cent respectively. The substance was probably not quite dry, but the agreement of the two results is satisfactory.
3. A sample of pure benzene hexachloride was found to contain 73.23 per cent of chlorine. The theoretical percentage for $C_6H_6Cl_6$ is 73.15.
4. Ten consecutive analyses of carefully dried hexachloro-benzene (Kahlbaum's), with theoretically 74.71 per cent chlorine, gave the following results:—

Percentage of chlorine found.	Error.
74.78	+0.07
74.71	—
74.78	+0.07
74.76	+0.05
74.62	-0.09
74.64	-0.07
74.69	-0.02
74.78	+0.07
74.71	—
74.75	+0.04

Taking into account the fact that the four substances used are among the most stable organic halogen compounds, these results may be considered as sufficient proof of the general applicability and accuracy of the method.

The investigation was carried out under the guidance of the Director of these Laboratories, Professor M. A. Rosanoff, whom the writer wishes to thank again for his friendly interest and assistance in the work. Acknowledgment is also due to Dr. W. L. Prager for his assistance in the early part of the work.

Clark University, Worcester, Mass.,
June, 1908.

THE APPLICATION OF THE COBALTI-NITRITE METHOD TO THE ESTIMATION OF POTASSIUM IN SOILS.

By W. A. DRUSHEL.

In a previous paper from the Kent Chemical Laboratory of Yale University it was shown that potassium may be estimated with a fair degree of accuracy by precipitating it as potassium sodium cobalti-nitrite in a solution acidified with acetic acid and oxidising the precipitate with standard potassium permanganate (*Am. Journ. Sci.*, 1907, xxiv., 433; *CHEMICAL NEWS*, xcvi., 124). In the same paper the applicability of the method to the estimation of potassium in commercial fertilisers was shown by a series of experiments.

In the method as previously worked out an excess of concentrated sodium cobalti-nitrite solution acidified with acetic acid is added to a neutral solution of a potassium salt, and the mixture is evaporated to a pasty condition on the steam-bath. After cooling, the residue is stirred up with sufficient cold water to dissolve the excess of sodium cobalti-nitrite. The precipitate, consisting of $K_2NaCo(NO_2)_6 \cdot H_2O$, is filtered on a rather close asbestos felt in a perforated crucible and well washed with cold water, or preferably with a half saturated sodium chloride solution. The precipitate and felt are transferred to an excess of standard N/10 or N/5 potassium permanganate which has been diluted to about ten times its volume and heated nearly to boiling. If particles of the precipitate stick persistently to the walls of the crucible and cannot be removed with a spray of water, the crucible is put into the permanganate solution. After stirring for a few minutes the solution is gradually acidified with 5 cc. to 20 cc. of dilute sulphuric acid, and the oxidation is allowed to go to completion, a process which seldom requires more than five minutes. If no particles of the yellow precipitate settle out on standing a minute, the oxidation may be considered complete. The hot solution is then bleached by running in a measured amount of standard oxalic acid, containing 50 cc. of concentrated sulphuric acid per litre. The solution after bleaching is titrated to colour with standard permanganate in the usual manner.

In this process the cobalt in the molecule is reduced from the trivalent to the bivalent condition and not re-oxidised, consequently from the molecule of the potassium sodium cobalti-nitrite we find 0.000857 grm. K_2O equivalent to 1 cc. of strictly N/10 potassium permanganate. This factor, of course, must be corrected for any variation in the normality of the permanganate solution used.

For the extraction of the alkalis 10 grms. of dry soil are placed in an Erlenmeyer flask with 25 cc. to 35 cc. of about 20 per cent hydrochloric acid. The flask is thoroughly shaken and a small funnel is hung in its neck to avoid too great a loss of acid by evaporation. The contents of the flask are digested on the steam-bath for twenty-four hours.

From this point several methods for the final preparation of the sample were tried with satisfactory results, given in the table. Since duplicate estimations were to be made by the gravimetric chlorplatinate method, for which it was

necessary to remove the iron, aluminium, calcium, magnesium, phosphoric acid, and ammonium salts, if present, from the soil extract, the following general procedure was found to be most expeditious. The soil extract was filtered through paper into an evaporating dish and the residue was washed with boiling water until the filtrate gave no reaction for chlorine with silver nitrate. The filtrate was evaporated almost to dryness to remove the excess of hydrochloric acid as far as possible. The residue was dissolved in about 200 cc. of water, and after heating to boiling, a little ammonium hydroxide and ammonium oxalate were added. The mixture was boiled a minute, settled, filtered, and the precipitate was washed with hot water until a drop of the filtrate gave no chlorine reaction. The filtrate was concentrated, transferred to a 200 cc. flask, cooled, and made up to the mark. After thoroughly shaking, 50 cc. aliquots were pipetted off for the gravimetric and volumetric estimations. The aliquots were evaporated to dryness in platinum dishes, and gently ignited to remove the ammonium chloride. After cooling, the residue was moistened with dilute sulphuric acid and again ignited, gently at first and finally at the full heat of the Bunsen flame, to remove the last trace of ammonium present as the sulphate, and to destroy any organic matter which might be present.

The residue for the gravimetric estimation was dissolved in a little water and a few drops of hydrochloric acid over the steam-bath, and the estimation of the potassium was made according to the modified Lindo-Gladding method.

To dissolve the residues for the volumetric estimations a little water and a few drops of acetic acid instead of hydrochloric acid were used. In the volumetric work approximately N/5 potassium permanganate was used, 26.08 cc. of permanganate being equivalent to 50 cc. of exactly N/10 oxalic acid. From this ratio the factor for K₂O was found to be 0.001642. In each case the potassium was precipitated as the cobalti-nitrite by evaporating off with 10 cc. of sodium cobalti-nitrite prepared according to the method of Adie and Wood (*Journ. Chem. Soc.*, lxxvii, 1076).

were removed in the separate aliquots by ammonium hydroxide and ammonium oxalate. In VII. the aliquots were made directly from the hydrochloric acid extract. That of VII. (2) was treated in the usual manner for the gravimetric estimation of potassium. The other aliquots of VII. were evaporated to dryness and gently ignited to remove any ammonium chloride present and to char the organic matter. The residues were extracted with hot water and a little acetic acid, filtered, and evaporated with sodium cobalti-nitrite in the usual manner.

In this work the results are based on a small amount of soil (2.5 grms.) in each case because but a limited amount of each sample was available. A higher degree of accuracy may be secured by using 10 grms. of soil for each estimation instead of 2.5 grms.

Summary.

A weighed amount of dry soil is extracted with an excess of hydrochloric acid over the steam-bath. The excess of acid is removed from the extract by evaporation. The bases which might interfere with the process are removed with sodium carbonate or ammonium hydroxide and ammonium oxalate. Ammonium salts and organic matter are removed by ignition. The residue is dissolved in a little water and a few drops of acetic acid, and the mixture evaporated with an excess of sodium cobalti-nitrite to a pasty condition, stirred up with cold water, and filtered upon asbestos in a perforated crucible. The precipitated potassium sodium cobalti-nitrite is washed with half-saturated solution of chloride, and treated with an excess of permanganate in hot dilute solution. The colour of the permanganate is destroyed by an excess of standard acidulated oxalic acid, and the excess of oxalic acid titrated to colour with permanganate.—*American Journal of Science*, xxvi., 329.

THE CORROSION OF IRON.*

By ALLERTON S. CUSHMAN,
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Introduction.

IN 1905 the Department of Agriculture published *Farmers' Bulletin* No. 239 on the subject of corrosion of fence wire. A large number of complaints had reached the Department from farmers in regard to the rapid corrosion of steel of modern manufacture used for various purposes, and especially for wire fencing. As the same difficulty has been constantly met in the use of corrugated iron and steel culverts for road drainage, it was decided to begin an investigation of the entire subject. The intention has been not only to get at the facts in the case, but also to aid as much as possible in bringing about an improvement in the rust-resisting quality of iron and steel used for the special purposes mentioned above.

Coincidentally with the beginning of the investigation inaugurated by the Office of Public Roads much attention began to be given to the same subject by a number of prominent metallurgists and chemists, both in this country and abroad. The American Society of Mining Engineers, at their Washington meeting, held in May, 1905, engaged in a discussion of the relative corrosion of iron and steel, and a vigorous debate followed the presentation of several papers on the same subject at the meeting of the American Society for Testing Materials, held at Atlantic City in June, 1906. The subject was considered so important that the latter Society appointed a Special Committee of ten members to make an investigation of it.

(NOTE.—Prof. W. H. Walker, of the Massachusetts Institute of Technology, a member of this Committee, has for some time past been making an independent investigation of the cause of the corrosion of iron. The writer

No.	Character of soil.	Method.	Soil taken. Grms.	K ₂ O found.	
				Grm.	Per cent.
I. Clay ..	(1) Vol.	2.5	0.0028	0.11	
	(2) " "	2.5	0.0035	0.14	
	(3) Grav.	2.5	0.0035	0.14	
II. Clay ..	(1) Vol.	2.5	0.0100	0.39	
	(2) " "	2.5	0.0092	0.37	
	(3) Grav.	2.5	0.0093	0.37	
III. Loam ..	(1) Vol.	2.5	0.0074	0.30	
	(2) " "	2.5	0.0068	0.27	
	(3) Grav.	2.5	0.0075	0.30	
IV. Loam ..	(1) Vol.	2.5	0.0060	0.24	
	(2) " "	2.5	0.0058	0.23	
	(3) Grav.	2.5	0.0058	0.23	
V. Gravel ..	(1) Vol.	2.5	0.0042	0.17	
	(2) Grav.	2.5	0.0045	0.18	
VI. Gravel ..	(1) Vol.	2.5	0.0047	0.19	
	(2) " "	2.5	0.0044	0.18	
	(3) Grav.	2.5	0.0050	0.20	
VII. Clay .. Gravel ..	(1) Vol.	2.5	0.0048	0.19	
	(2) Grav.	2.5	0.0046	0.18	
	(3) Vol.	2.5	0.0045	0.18	
	(4) " "	2.5	0.0040	0.16	
	(5) " "	2.5	0.0044	0.18	

The following exceptions are to be noted to the general method previously outlined for the preparation of the sample. In I., the excess of hydrochloric acid, the iron, aluminium, and calcium were removed from the separate portions after aliquoting, and in (1) and (2) sodium carbonate was used instead of ammonium hydroxide and ammonium oxalate for the removal of the iron, aluminium, and calcium. In V. (1) and (2) bases other than the alkalis

* *Bulletin* No. 30, U.S. Department of Agriculture, Office of Public Roads.

has reason to believe that the results of Prof. Walker's work will be found to confirm in a large measure the observations recorded in this *Bulletin*. Although contemporaneous, the two investigations have been carried on quite independently, except in regard to the development of the ferroxy indicator).

In the *Farmers' Bulletin* mentioned above, on the corrosion of fence wire, special attention was given to the subject of electrolysis and its effects on wire. The suggestion was made that lack of homogeneity in the distribution of impurities in metal made by rapid modern processes might be at the bottom of the trouble. Some objection has been raised to this suggestion on the ground that, although electrolysis probably plays a large part in the rusting of water-pipes and structural iron in the neighbourhood of electric conduits, it is unlikely that it can be considered a prime cause of the rusting or corrosion of iron and steel under all circumstances. Nevertheless, acting on the suggestion made in this *Farmers' Bulletin*, some of the manufacturers have made a determined effort to turn out a metal more resistant to corrosion, and the present indications are that these efforts have not been unsuccessful.

In 1894 and 1895 a series of papers, under the title "Rustless Coatings for Iron and Steel," was contributed by M. P. Wood to the *Transactions of the American Society of Mechanical Engineers* (1894, xv., 998; 1895, xvi., 350, 663). In these papers all that was known up to that time on the cause and cure of corrosion is presented and ably discussed. On page 1070 of the *Transactions* for 1894 this author states:—

"That there is a continual electrical action of a most complex character present in all boilers under steam can scarcely be doubted, and the same action, but less apparent, is possibly present in all constructions of iron when the different members formed of iron and steel of various compositions, made by different processes after various torturing methods of manufacture to bring them to the desired shape, are assembled and put into duty under strains and conditions foreign to their nature. It would be strange indeed did not some electrical energy manifest itself and call for some palliative if not protective means of arresting decay."

It is well known that the various kinds of merchantable iron and steel differ within wide limits in their resistance, not only to the ordinary processes of oxidation known as rusting, but also to other corrosive influences. It is also true that different specimens of one and the same kind of iron or steel will show great variability in resistance to corrosion under the conditions of use and service. The causes of this variability are undoubtedly numerous and complex, and it is safe to say that the subject is not nearly so well understood at the present time as it should be.

In regard to two points all investigators are agreed, and as these furnish at least some common ground it is interesting to record them before proceeding to a discussion of the points at issue. Iron cannot rust in air or oxygen unless water is present, and, on the other hand, it cannot rust in water unless oxygen is present. An interesting summary of the opinions held by various authorities prior to 1903 has been given by Mugdan (*Zeit. Elektrochemie*, 1903, ix., 442), but although a number of investigators have worked on the problem since that time, the fundamental reactions which take place when a bright strip of iron immersed in water becomes coated with the red hydroxide known as rust are still a subject of controversy.

Three separate theories which, though they all more or less overlap, nevertheless involve distinctly different reactions, have been advanced and strenuously defended in the effort to furnish an explanation for the rusting of iron. These may be stated as the carbonic acid, the hydrogen peroxide, and the electrolytic theories.

Before any distinct progress can be made in the manufacture of metal that shall be more than ordinarily resistant to corrosion, it is of great importance that the underlying causes of oxidation should be clearly understood. It is

the object of this paper to discuss the different theories and to present certain evidence recently obtained which bears directly upon the subject.

The Carbonic Acid Theory.

The carbonic acid theory is the one most generally held, and usually presumes that without the interaction of carbonic or some other acid the oxidation, or better, the hydroxylation, of iron cannot take place. The theory is best set forth in the words of a text-book recently published (Treadwell and Hall, "Analytical Chemistry," 1907, p. 92):—

"The process of rusting is a cyclical one, and three factors play an important part:—(1) An acid, (2) water, (3) oxygen. The process of rusting is always started by an acid (even the weak carbonic acid suffices). The acid changes the metal to a ferrous salt with evolution of hydrogen: $2\text{Fe} + 2\text{H}_2\text{CO}_3 = 2\text{FeCO}_3 + 2\text{H}_2$.

Water and oxygen now act upon the ferrous salt, causing the iron in this salt to separate out as ferric hydroxide, setting free the same amount of acid which was used in forming the ferrous salt: $2\text{FeCO}_3 + 5\text{H}_2\text{O} + \text{O} = 2\text{Fe}(\text{OH})_3 + 2\text{H}_2\text{CO}_3$.

The acid which is set free again acts upon the metal, forming more ferrous salt, which is again decomposed, forming more rust. A very small amount of acid therefore suffices to rust a large amount of iron. If the acid is lacking, the iron will not rust. If we desire to prevent this rusting, we must neutralise the acid, e.g., add milk of lime. Iron remains bright under an alkali."

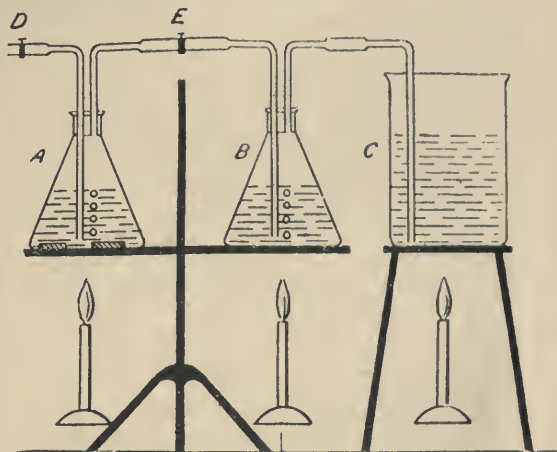


FIG. 1.—APPARATUS TO SHOW THE ACTION ON IRON OF PURE WATER AND OXYGEN.

Probably no better example than this could be cited to show the text-book tendency to supply a complete explanation of a well-known phenomenon, the underlying causes of which are still imperfectly understood. Although the above explanation is sufficiently plausible, and in spite of the fact that carbonic acid, as well as other acids, do act a part in the ordinary rusting of iron, it will presently be shown that iron readily oxidises, not only when carbonic acid is entirely absent, but also in dilute alkaline solutions. It is only when the hydroxyl ions supplied by an alkaline solution have reached a certain concentration that rusting is entirely prohibited.

The carbonic acid theory was founded originally on the investigations of Crace Calvert (*Mem. Manchester Lit. Phil. Soc.*, 1871, v., 104), as interpreted by Crum Brown (*Journ. Iron and Steel Inst.*, 1888, p. 129). It has also more recently been vigorously defended by Moody (*Proc. Chem. Soc.*, 1906, xxii., 101), who insists that with water and oxygen quite free from carbonic acid iron cannot rust. This view is, however, not shared by Dunstan, Jowett, and Goulding (*Journ. Chem. Soc.*, 1905, lxxxvii., Part II.,

1548), or by Whitney (*Journ. Am. Chem. Soc.*, 1903, xxv., 394) or Cribb (*The Analyst*, 1905, xxx., 232), all of whom give experimental evidence to show that rusting takes place rapidly in the absence of carbonic acid, provided liquid water and oxygen are present. The experiment of Dunstan and his co-workers was so carefully carried out that there seems to be no doubt that if carbonic acid plays any rôle whatever it is an unimportant one, and that rusting can go on with extreme rapidity in its absence.

In order to confirm this conclusion, the following experiment was made by the writer:—

The Jena glass flasks A, B, and the beaker C, shown in Fig. 1, were nearly filled with freshly distilled water, and boiled vigorously for one half-hour. While the boiling was still proceeding bright polished strips of charcoal iron and steel were slipped into flasks A and B, and the rubber stoppers, which had been previously cleaned by prolonged boiling in pure water, tightly inserted. After boiling for fifteen minutes longer the clamp at the end of tube D was opened for a moment, and the back pressure allowed to drive any last traces of air from the tube. After tightly closing the clamp again, the lamps under flasks A and B were removed, while the water in C was still kept boiling. Boiled water immediately sucked back until the whole apparatus was completely filled, no trace of air being present. At all events, no slightest trace of rust appeared on the bright metal strips when kept indefinitely under this boiled water. Pure oxygen from a cylinder was now washed perfectly free from last traces of carbonic acid by passing the gas through a train of wash-bottles containing caustic potash, barium hydroxide, and lime-water. On allowing this carefully purified oxygen to enter at D and bubble through the system of flasks, rust appeared on the bright metal surfaces in five minutes or less, and in one hour had become deep and heavy. The action, just as in Dunstan's experiments, did not take place evenly all over the surface, but in patches, which had the appearance of a more or less regular pattern following the physical structure of the metal. This experiments has been frequently repeated, with every possible precaution to avoid the entrance of even the smallest trace of carbonic acid. On numerous occasions a few drops of phenolphthalein indicator was added to the boiling water in the three flasks, and invariably a pink colour developed, proceeding from the metallic surfaces. This effect will be discussed at length further on, and is mentioned at this place as contributory evidence that carbonic acid is not necessarily present, as Moody believes, before any reaction between iron, water, and oxygen can take place.

If pure dry carbonic acid gas, freed from oxygen by passing through several wash-bottles containing pyrogallol acid dissolved in sodium bicarbonate solution, was substituted for the pure oxygen gas and allowed to enter through tube D, no perceptible action took place on a bright piece of steel after several hours, although there can be no doubt that iron passed to a slight extent into solution as ferrous carbonate. Finally, if pure oxygen was allowed to enter at the same time and mingle with the carbonic acid, corrosion began in a short time. There was, however, a difference in the appearance of the rust that was formed with and without the interaction of carbonic acid. In the presence of carbonic acid the characteristic blue-green gradually changing to the red colour peculiar to rust was observed. This appearance, as Moody truly observes, invariably accompanies the early stage of attack when iron is rusting in the presence of carbonic acid. In the experiments in which pure oxygen alone was permitted to enter the apparatus the blue-green initial stage of oxidation was never observed, the red ferric hydroxide making its appearance from the first, as it usually does, in normal cases of atmospheric rusting of bright iron surfaces.

It may be doubted whether it is possible to boil out all carbonic acid from the water contained in the apparatus shown in Fig. 1. Granting that this is the case in regard

to last traces, it is easily shown that the hydrogen ions which would be supplied by a minute quantity of carbonic acid are of no more importance than the hydrogen ions supplied by the normal dissociation of pure water, and that the assumption that carbonic acid must be present is quite unnecessary. Whitney (*Journ. Am. Chem. Soc.*, 1903, xxv., 397) shows this very clearly in the following paragraph:—

"Assuming the laws of Henry and Dalton to apply to the solubility of carbonic acid gas in water, also that the solubility of the pure gas under ordinary pressure is one volume for one volume of water (which is correct at 15° C.), and, finally, that the normal content of carbonic acid in the atmosphere is 2 parts in 10,000 by volume, we should expect water in equilibrium with air containing this concentration of carbonic acid to contain 0.0002 volume carbon dioxide per volume of water. This corresponds to a concentration of the carbonic acid equal to 0.00001 mol. per litre, or 0.00002 normal. From the dissociation constant 3040×10^{-10} determined by Walker (*Zeit. Phys. Chem.*, 1900, xxxii., 137), it follows that the first hydrogen of the acid is 16 per cent dissociated at this concentration. From this it follows that 10,000,000 litres of water containing carbonic acid in equilibrium with ordinary air at 15° contains 16 grms. of hydrogen ions, or only sixteen times as many as perfectly pure water contains. At the boiling temperature the carbon dioxide dissolved would probably yield a concentration of hydrogen ions even less than in pure water, for not only is the solubility of the gas greatly diminished, but the dissociation of water is greatly increased by rise of temperature. Moreover, the distilling water would rapidly reduce the concentration of any carbonic acid capable of dissolving in water at 100° C."

Moody prepared an apparatus in which the presence or subsequent entrance of even the smallest traces of carbonic acid was elaborately guarded against. The apparatus was constructed entirely of glass, and was arranged in such a manner that polished cylinders of almost pure soft Swedish iron could be subjected to the action of water, and air absolutely free from carbonic acid. Even with the very pure iron and with water which was undoubtedly rendered slightly alkaline by its intimate contact with a large surface of ordinary glass, Moody observed a slight amount of corrosion taking place on his bright iron surfaces. Still convinced, however, that the presence of carbonic acid was necessary before the slightest rusting effect could be produced, and believing that in some unknown manner an infinitesimal amount of this substance had eluded his vigilance, Moody began again with a new and quite extraordinary precaution. Before the bent tube, which contained the polished specimen of iron was fused into its place in the apparatus, it was partly filled with a 1 per cent solution of chromic acid which just covered the iron. When the apparatus had been swept with air free from carbonic acid for three weeks, water was distilled through the tube containing the specimen until the chromic acid was all washed away. After this, as well as the added precaution of covering the ends of the iron cylinders with wax to prevent contact with the glass (as an interaction between glass and iron appeared also to cause corrosion even if no carbonic acid was present), the experiment was finally a complete success. In one case a current of air was passed through the apparatus for five weeks without even one speck of rust appearing.

If Moody's experiment could be accepted as final, we must conclude that in an atmosphere that did not, like that of this earth, contain about 0.04 per cent of carbonic acid, the rusting of iron would be an unknown phenomenon.

It happens, however, that a recent observation of the writer explains the negative result obtained by Moody, without any reference whatsoever to the carbonic acid theory of rusting. It has long been known that rusting is inhibited, and that polished iron will remain bright indefinitely in alkaline solutions, provided they are sufficiently concentrated. This is also true of all solutions of

salts of strong bases and weak acids which hydrolyse to an alkaline reaction (*Zeit. Elektrochemie*, 1903, ix., 446). This fact has been eagerly seized upon by the adherents of the three theories, as it can be made to fit in more or less well with them all. Thus, alkalis absorb carbonic dioxide, and therefore carbonic acid is prevented from carrying on its work of destruction. The added fact that fully saturated bicarbonate of soda also provides full protection to iron, even in fairly dilute solution, which would seem to be a stumbling block, has not shaken the faith of the devout believers in the carbonic acid theory.

The adherents of the peroxide theory claim that iron cannot rust unless hydrogen peroxide is formed as a transition step in the reactions. As hydrogen peroxide is more or less unstable in alkaline solutions it is claimed that iron should not rust when immersed in them. The added fact that the rusting of iron is actually accelerated by solutions of potassium iodide, iodine, dilute potassium permanganate, and other substances which also destroy hydrogen peroxide, must apparently be accepted as an exception which proves the rule. The theory of electrolysis alone finds no difficulty in appropriating the facts of the alkali inhibition of oxidation. The full discussion of this point, however, must be postponed to a later portion of this *Bulletin*.

As far as the writer is aware, Dunstan and his co-workers were the first to make use in a theoretical discussion of the fact that solutions of chromic acid, potassium chromate, and potassium bichromate exercise a complete protection from rust to the surfaces of iron specimens immersed in them. It is probable, however, that the protective power of the chromates and some other oxidising agents has been known, and to some extent made use of, in a practical way for a long time past (*Trans. Am. Chem. Soc. Eng.*, 1894, xvi., 384). Wood stated in 1894 that a few substances, such as red-lead, pyrolusite, the bichromate of potash, and chromate of lead, were gradually coming into use for anti-corrosive paint compounds, and that their future use for this purpose was assured. This peculiarity of the chromates was interpreted by Dunstan as furnishing a proof of the peroxide theory, as it is well known that hydrogen peroxide is destroyed by chromic acid and its salts.

The writer has gone a step further, and observed that the protection afforded by chromic acid and its salts differs from that of the alkalis in that the passivity is in a sense acquired by the surface of the iron, and lasts for long periods, although the chromated specimens may have been washed with all possible care, and even wiped with a cloth. In the writer's experiments all chromating has usually been done by immersing polished specimens of iron and steel in a strong solution of potassium bichromate for a number of hours, generally over-night. Steel-wire nails treated in this way have been kept under water in vessels open to the contact of air and carbonic acid for many weeks without developing the slightest speck of rust or tarnish on their polished surfaces. In addition to this, polished specimens which have been chromated have been kept in moist air for weeks at a time without losing their passive condition. This astonishing phenomenon is so easily and quickly demonstrated by any one who cares to make a trial of it that it is not necessary in this place to include evidence to support the statement made above. The subject will be taken up in detail later on, and it is only mentioned here to show that Moody's experiment does not prove that the presence of carbonic acid is necessary before iron can rust. It must, of course, be admitted that the presence of hydrogen ions will hasten the corrosion of iron, and therefore the presence of a small amount of carbonic acid plays a minor rôle. The point that is made is that carbonic acid is not necessary, and that rusting can go on with extreme rapidity without it. If Moody had used pure oxygen instead of air he would undoubtedly have rusted his specimens in spite of their having been first chromated.

(To be continued).

NOTICES OF BOOKS.

A Treatise on Colour Manufacture. By GEORGE ZERR and Dr. R. RÜBENCAMP. Authorised English Edition by Dr. CHARLES MAYER. London: Charles Griffin and Co., Ltd. 1908.

THE German edition of this work was a book whose merits were immediately recognised, and one which met with much success; no doubt the English version will be equally appreciated, for though small alterations have been made, in the main it reproduces very faithfully the good features of the original. The different colouring matters are classified according to a convenient system, and each individual substance is given thorough treatment, some notes being occasionally added by the translator. A short summary is given of the coal-tar colours, and also some account of the uses of colours, which, however, is perhaps too much condensed to be of any practical good to the specialist. It is unfortunate that some very important recent advances, as in the analyses of lake pigments, are not described in the text, although in many cases the translator calls attention in a footnote to books and articles which may be consulted for the most recent information.

Technical Methods of Chemical Analysis. Edited by GEORGE LUNGE, Ph.D., Dr. Ing. English Translation Edited by CHARLES ALEXANDER KEANE, D.Sc., Ph.D. Volume I., Parts I. and II. London: Gurney and Jackson. 1908.

THE English translation of this standard work on chemical analysis has been prepared from the second German edition, issued in 1904, and in many respects it must be regarded as a unique production. Each section, which was written by an expert in the first case, and represented the last word on analytical practice in Germany, has again been revised by an expert who has a special knowledge of the conditions of English manufacture where they differ from those which hold in Germany, and of the requirements of English chemists. The references to literature have been altered so that English books and articles are substituted for German, and where necessary the text has been brought up to date by Prof. Lunge and the English editor. The treatise fulfils a double purpose, being both a work of reference, summarising all well-established methods of analysing the raw materials, intermediate, and final products of the different industries, and also a practical laboratory guide describing the performance of the most satisfactory methods in the case of each substance. Volume I. has been issued in two parts, which contain, firstly, a complete introduction to chemical analysis, discussing all the methods employed with full details of the operations with which the chemist should be familiar. In addition many important groups of industries are treated, including the manufacture of acids, salt-cake, sodium carbonate, clay, glass, &c., while the analyses of air, water, sewage, soils are among the subjects treated in the second part.

Catalogue of Balances and Weights. London: F. E. Becker and Co. (W. and J. George, Ltd., successors). 1908.

THIS new balance catalogue is so excellently illustrated, and all the apparatus enumerated in it is described with such careful attention to every important detail, that no customer need entertain any doubt about the wisdom of ordering an article without having actually seen and handled it. The firm is renowned for the reliability and good finish of the instruments they put upon the market, and their prices must be acknowledged to be surprisingly low in some cases, especially when it is remembered that the name Becker is a guarantee of accuracy and good wearing properties. Various forms of specific gravity and

spring balances are illustrated in the catalogue, and, in addition, all accessories are listed, including forceps, spirit levels, sets of weights, and triangular calcium chloride vessels.

Catalogue of Apparatus for Chemical Lecture Experiments. London: A. Gallenkamp and Co., Ltd. 1908.

THIS catalogue of apparatus for chemical lecture experiments contains a price list of the whole range of Hofmann's and Newth's lecture apparatus with some valuable additions, and full descriptions are given of some of the instruments with directions for their manipulation. The time of the chemical lecturer or demonstrator will be much economised by the use of some of this apparatus, which is comparatively inexpensive, while sometimes troublesome to fit up from the ordinary laboratory stores. Attention must be called to the description of an optical lantern for horizontal and vertical projection, which would appear to be a thoroughly satisfactory instrument.

A Scheme for the Promotion of Scientific Research. By WALTER B. PRIEST. Second Edition. London: Stevens and Sons, Ltd. 1908.

THE second edition of this book is a reprint of the first, except that it contains some fuller explanations and details, more especially of the question of assessment in the author's scheme for endowing scientific research. The plan seems workable, and in view of the excellence of the object which it aims at promoting, it would perhaps be invidious to lay too much stress on obvious defects and difficulties which are chiefly concerned with the assessment of the grants to be made. The author regards discoveries by which the mortality arising from various diseases may be lowered as deserving special attention and most liberal recognition, but the scheme might easily be extended to other fields of research. The procedure recommended is based upon the Patents Act of 1883, sections and sub-sections of which are quoted in an appendix. The author writes with moderation, and it seems probable that the adoption of his scheme would give an impetus to scientific research, and thus benefit civilisation.

Cours de Chimie Inorganique. ("Course of Inorganic Chemistry"). By FRED. SWARTS. Paris: A. Hermann. 1908.

THIS book occupies an intermediate position between those text-books which are rigidly divided into two parts—*theoretical and descriptive*—and the more modern ones in which the treatment corresponds to the heuristic oral method of teaching, and theories are only suggested to explain facts which have already been observed or studied. Thus it belongs to the old type in that in a general introduction the atomic and other fundamental theories are discussed, while descriptions of the properties, preparation, &c., of each individual element follows. But, on the other hand, throughout the descriptive part are to be found discussions of the theoretical aspects of the various phenomena considered. The book is based upon the course of chemistry for engineering students at the University of Gand, and is thus not intended for the use of young beginners. Although it is perhaps not a work which a student could be advised to read straight through, it is in many ways not unsuitable for him if he has the advantage of having a competent teacher to decide in what order the chapters are to be read. The student will find the frequent heavy type and the short paragraphs employed are helpful, and, on the whole, he will be able to gain from the book a very fair notion of descriptive chemistry, including some metallurgy and industrial processes. One chapter is given to thermochemistry and is a good feature, but a serious defect is the omission of all allusion to the Periodic System. It is now generally recognised that an outline of the main features of the system give interest to the study of

inorganic chemistry, and enable greater calls to be made upon the students' deductive powers and less upon his memory—thus tending to remove a reproach from the science as an educative subject. Moreover, the generalisations of the Law give the beginner a much sounder knowledge of chemistry than he can get from the study of isolated and apparently unconnected reactions and properties

Salpeter und sein Ersatz. ("Saltpetre and its Substitutes"). By KONRAD W. JURISCH. Leipzig: S. Hirzel. 1908.

THE growth in importance and magnitude of the chemical industries connected with the artificial production of nitrogenous manures demands new books dealing with them, and this treatise on saltpetre is, no doubt, the forerunner of many similar works. The first part of it deals with the extraction, preparation, analysis, &c., of ordinary and Chili saltpetre; methods of analysis are given only in outline, and certain by-processes, such as the preparation of nitric acid, the chemistry and technology of ammonia, are not discussed, but full bibliographies, dating in one case from 1895 and in the other from 1830, of the literature of the subjects in all languages are given, together with some additional notes on important articles and books. The needs of plants as regards nitrogenous manures are discussed in some detail, and illustrations of the influence of different manures on the growth and development of plants are reproduced. The preparation and properties of calcium cyanamide are treated fully, and also the production of nitric acid from the air. The different factories which have sprung up in Norway are described and illustrated, and the rapid growth of this particular industry is made very evident.

Kolloidchemische Studien am Eiweiss. ("Studies in Colloidal Chemistry with Albumen"). By W. PAULI. Dresden: Theodor Steinkopff. 1908.

THIS monograph is a reprint of a lecture which was delivered in Vienna in June, 1908, and published in the July number of the *Zeitschrift für Chemie und Industrie der Kolloide*. Its issue as a separate publication is justified by the admirable survey it gives of the author's valuable researches on albuminous substances and the effects of salts upon them. These researches, which led to some results of the greatest importance, were ably conceived and skilfully performed, and were specially aimed at the reproduction of the conditions which obtain in the living organism, so that their application to the solution of physiological problems is at once apparent. One of the most important results obtained was the demonstration that the ions of neutral salts form adsorption compounds with albuminous substances, a theory which was put forward some time ago by the author and Prof. Loeb. Besides describing the experimental arrangements and the conclusions to be drawn from the results obtained, the author discusses briefly the bearing of his own and other investigators' work on physiological problems; he holds the view that the albuminous constituents of the plasma are the substances which are first attacked by the ionised compounds.

MEETINGS FOR THE WEEK.

MONDAY, 4th.—Society of Chemical Industry, 8. "Cinchonamine and certain other Rare Alkaloids," by B. F. Howard and O. Chick. "Theory of Dyeing," by W. P. Dreaper. "A Physico-chemical Method for comparing the Antiseptic Value of Disinfectants," by S. B. Schryver and R. Lessing.

TUESDAY, 5th. } Royal Institution, 3. (Christmas Lectures
THURSDAY, 7th. } adapted to a Juvenile Auditory). "The Wheel
SATURDAY, 9th. } of Life," by Prof. W. Stirling, M.D., &c.

WEDNESDAY, 6th. } Royal Society of Arts, 5. (Juvenile Lecture).
"Digging for Ancient Art Treasures," by Chas. Waldstein.

THE CHEMICAL NEWS.

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MEASUREMENT OF ROTATORY DISPERSIVE POWER IN THE VISIBLE AND ULTRA-VIOLET REGIONS OF THE SPECTRUM.*

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THE following is a brief preliminary account of improvements effected in the method of determining rotatory dispersive power which have made it possible to observe accurately not only in the bright regions of the visible spectrum, but throughout the scale from the region of the lithium red line into that commanded by the photographic plate.

Two methods have generally been used for the purpose, namely, (1) Broch's method, in which a spectroscope is arranged in series with the polarimeter and a narrow strip of a continuous spectrum is picked out for observation—a method which is much improved by using a constant-deviation spectroscope in place of one of the variable-deviation type (F. Twyman, *Phil. Mag.*, 1907, xiii., 481), and (2) Landolt's method, in which a white light is reduced by means of filters to approximate homogeneity in the red, green, light blue, or dark blue parts of the spectrum. Neither method fulfils the fundamental condition that the field of the polarimeter shall be uniformly lighted with monochromatic light—many of the measurements that have been made, therefore, possess only a qualitative value. A much better method is due to the late Sir William Perkin, who introduced the use of a spectroscope-eyepiece as a means of purifying the sodium light, and used it on a limited scale for measuring rotatory dispersive power in the red (lithium), yellow (sodium), and green (thallium) parts of the spectrum.

The method now described resembles Perkin's method in its essential feature, namely, the use of monochromatic or multichromatic light (spectroscopically purified) in place of a band from a continuous spectrum. It has the advantage that it renders available for polarimetric measurements, in addition to the flame spectra, the large series of intense line spectra produced by the metallic arcs, which, with the one exception of the enclosed mercury arc (Disch, *Ann. Phys.*, 1903, [4], xii., 1155), do not appear to have been used previously for this purpose. Up to the present, measurements have been made with 26 lines ranging from wave-length 6708 to 4359; beyond these limits the visual intensity of the light is so small that polarimetric observations become very difficult, but in the intermediate part of the spectrum the list might, without difficulty, be extended considerably. The mercury lines referred to in the table were produced by a Bastian lamp; the copper and zinc spectra were produced by means of copper or brass electrodes rotating in opposite directions, as recommended by Baly in the case of the iron arc; the cadmium spectrum was obtained by means of rotating copper or silver electrodes coated with the metal.

In order to utilise the arc spectra for polarimetric observations, a parallel beam from the arc is thrown on to the widely-opened slit of a constant deviation spectroscope. An achromatic lens of 22" focus is substituted for the observing telescope of the spectroscope, and is used to cast a magnified image of the slit on to the polarising prisms which produce the horizontally-divided triple field of the polarimeter. By turning the constant-deviation prism to a suitable position, the field can be illuminated from top to bottom by a brilliant band of pure monochromatic light, the maximum width of the band being

determined by the openness of the spectrum and, in a very important manner, by the efficiency of the dispersive system. By using a C.D. prism of high density in conjunction with the long-focus lens, it is possible to read separately the two lines 5790 and 5769 which constitute the yellow mercury doublet, although these differ in wave-length by only 21 Angström units; the yellow doublet and green triplet in the copper spectrum can be read with ease and accuracy as broad bands each occupying a width rather greater than one-third of the 8 mm. aperture of the triple field; the chief lines in the mercury and cadmium spectra can be made to cover practically the whole field without overlapping. In order to eliminate stray light, which would give rise to serious errors in the red and violet readings, a Perkin spectroscope eye-piece is used.

In measuring rotatory dispersive power in the ultra-violet, a parallel beam of light from an arc formed between a carbon and a magnetite electrode is cast directly by a quartz condenser on to the triple field of the polariser, Foucault prisms being substituted for the Nicol prisms to ensure transmission. A quartz-calcite lens of 13" focus is substituted for the analyser-telescope; this casts a diminished image of the triple field on the slit of an ultra-violet spectroscope. The spectrum thus produced is photographed in the ordinary way by means of a camera provided with a quartz-calcite lens of 22" focus; the division produced by the triple field can be seen clearly, and it is easy to pick out and identify on the negative the line which is of equal intensity in its three sections. By taking photographs with the analyser in different positions it is possible to determine the rotatory power of a substance throughout the transmitted spectrum.

The results obtained with water, carbon bisulphide, and other liquids in a magnetic field will be dealt with in a later communication; the method is one which is likely to be of special value as affording a means of determining the homogeneity of apparently simple liquids. In the table below the results are reliable within two or three units in the last figure.

The polarimeter readings shown in the table were usually concordant within a few hundredths of a degree; the absolute values may differ by as much as 1° in different specimens of the ester, but the relative values, $\alpha/\rho D$, are probably reliable within one or two units in the last figure.

Table of Wave-lengths used in the Measurement of Rotatory Dispersive Power, together with the Rotations produced by 100 mm. of Methylc Camphocarboxylate at 20° C.

	Wave-length.	α .	$\alpha/\rho D$.
Li red	6708	48°32'	0·728
Cd red	6438	53°41'	0·805
Zn red	6364	54°91'	0·827
Na yellow . . .	5893	66°37'	1·000
Hg yellow . . .	5790	69°40'	1·046
Cu yellow . . .	5782	69°83'	1·052
Hg yellow . . .	5769	70°09'	1·056
Cu yellow . . .	5700	72°38'	1·090
Ag green	5469	80°75'	1·217
Hg green	5461	80°94'	1·220
Tl green	5351	85°59'	1·290
Cu green	5219	91°73'	1·382
Ag green	5209	92°17'	1·389
Cu green	5154	94°93'	1·430
Cu green	5105	97°52'	1·469
Cd green	5086	98°60'	1·486
Zn blue	4811	116°15'	1·750
Cd blue	4800	116°93'	1·762
Zn blue	4722	122°92'	1·852
Cu blue	4705	124°38'	1·874
Zn blue	4680	126°36'	1·904
Cd blue	4678	126°55'	1·907
Cu blue	4651	128°34'	1·933
Cu blue	4587	134°60'	2·028
Cu violet	4378	157°62'	2·375
Hg violet	4359	165°07'	2·487

* A Paper read before the Royal Society, November 19, 1908.

THE SPECTRUM OF SCANDIUM AND ITS RELATION TO SOLAR SPECTRA.*

By A. FOWLER, A.R.C.S., F.R.A.S., Assistant Professor of Physics,
Imperial College of Science and Technology, South Kensington.

The greater part of this investigation of the spectrum of scandium under different experimental conditions has been based on purified scandia, generously placed at the author's disposal by Sir William Crookes. The principal results are as follows:—

1. The arc spectrum of scandium consists of two distinct sets of lines, which behave very differently in solar spectra. Each set includes both strong and faint lines.

2. Lines belonging to one set correspond with the enhanced lines of other elements, notwithstanding that they appear strongly in the ordinary arc spectrum—

- These lines are very feeble or missing from the arc-flame spectrum, and are strengthened in passing to the arc, the arc in hydrogen, or the spark.
- They occur as relatively strong lines in the Fraunhofer spectrum.
- They are weakened in the sun-spot spectrum.
- They occur as high-level lines in the chromosphere.

3. The remaining lines show a great contrast when compared with the first group—

- They are relatively strong lines in the arc-flame.
- They are very feebly represented in the Fraunhofer spectrum.
- The stronger lines are prominent in the sun-spot spectrum.
- They have not been recorded in the spectrum of the chromosphere.

4. The special development of the enhanced lines in the Fraunhofer spectrum, together with their presence in the upper chromosphere, indicates that the greater part of the scandium absorption in the solar spectrum originates at a higher level than that at which the greater part of the iron absorption is produced.

5. The discussion of scandium lines indicates that while in the case of some elements solar identifications are to be based chiefly on arc lines, in others it is the enhanced lines which may be expected to show the most important coincidences.

6. The flutings which occur in the arc and arc-flame do not appear when the arc is passed in an atmosphere of hydrogen. As suggested by Thalén, they are probably due to oxide of scandium.

Tables are given which show the lines of the arc spectrum from 3930 to 6580, the positions of the oxide flutings, and comparisons of the principal lines of the two classes with the sun, sun-spots, and chromosphere.

Decomposition of Diazo Solutions.—A. Hantzsch and K. J. Thompson.—After diazonium chlorides have been left for a long time in the desiccator, or dry air has been passed over them, they give the maximum value of the velocity of decomposition in aqueous solution. Freshly prepared solutions decompose more slowly and seem to contain some unknown substance which hinders decomposition. Dilute bromide solutions decompose at the same rate as the chloride. The velocity of decomposition increases very slowly with the concentration, that of the bromide solution rather more quickly than the chloride. Diazoiodide solutions even when very dilute decompose much quicker, and nitrobenzene diazonium solutions also decompose rather more quickly in very concentrated solutions; acids do not affect the decomposition of the last named compounds.—*Berichte*, xli., No. 14.

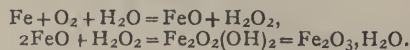
THE CORROSION OF IRON.*

By ALLERTON S. CUSHMAN,
Assistant Director, Office of Public Roads, Dept. of Agriculture, U.S.A.

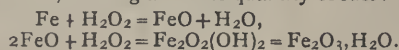
(Continued from p. 11).

The Peroxide Theory.

DUNSTAN, Jowett, and Goulding based their peroxide theory of the rusting of iron on the general well-known theory of oxidation advanced by Traube (*Ber.*, xviii., 1881). Thus the chemical reactions concerned in the formation of iron rust should be written:—



The excess of hydrogen peroxide immediately reacts with the iron, forming a further quantity of rust:—



Some of the evidence brought forward to substantiate this theory has already been referred to in a previous paragraph. It appears to derive some confirmation from the fact that delicate tests for hydrogen peroxide have been obtained during the slow oxidation of zinc and some other metals. On the other hand, in the case of iron these same delicate tests obstinately refuse to reveal even its transitory presence during the ordinary process of rusting. The theory has been criticised by Divers (*Proc. Chem. Soc.*, 1905, xxi., 251), Moody (*Journ. Chem. Soc.*, 1906, lxxxix. —cx., 720), and Cribb (*Analyst*, 1905, xxx., 225)—the first-named having pointed out that it is not tenable to argue that, because such substances as chromic acid and alkalis gradually destroy hydrogen peroxide, they must prevent its formation. For instance, ferrous sulphate is oxidised by free chlorine, but it does not prevent manganese dioxide and hydrochloric acid from reacting when brought together in its presence. Moreover, if the formation of hydrogen peroxide was a necessary stage in the rusting of iron, and this is inhibited by certain substances which destroy hydrogen peroxide, why is not the inhibition extended to strong reducing agents generally? The theory is an interesting and suggestive one, but in the author's opinion is not supported by the facts.

The Electrolytic Theory.

From the standpoint of the modern theory of solutions, all reactions which take place in the wet way are attended with certain re-adjustments of the electrical states of the reacting ions. The electrolytic theory of rusting assumes that before iron can oxidise in the wet way it must first pass into solution as a ferrous ion. The subject has been interestingly treated by Whitney (*loc. cit.*, p. 10), who discussed it from the standpoint of Nernst's conception of the source of electro-motive force between a metal and a solution. When a strip of metallic iron is placed in a solution of copper sulphate, iron passes into solution and copper is deposited, this change being of course accompanied by a transfer of electrical charge from the ions of copper to those of iron. Hydrogen acts as a metal, and is electrolytically classed with copper in relation to iron. If therefore we immerse a strip of iron in a solution containing hydrogen ions, an exactly similar reaction will take place, iron will go into solution, and hydrogen will pass from the electrically charged or ionic to the atomic or gaseous condition. In such a system the solution of the iron, and therefore its subsequent oxidation, must be accompanied by a "precipitation" or setting free of hydrogen. It is very well known that solutions of ferrous salts as well as freshly precipitated ferrous hydroxide are rapidly oxidised by the free oxygen of the air to the ferric condition, so that if the electrolytic theory can account for the original solution of the iron the explanation of rusting becomes an exceedingly simple one.

* Abstract of a Paper read before the Royal Society, June 25, 1908.

* *Bulletin* No. 30, U.S. Department of Agriculture, Office of Public Roads.

As iron has been shown by Whitney, Dunstan, and the writer to rust in the presence of pure water and oxygen alone, the electrolytic theory as a fundamental cause of the wet oxidation of iron must stand or fall on the determination of one crucial question, viz.:—Does iron pass into solution, even to the slightest extent, in pure water? If iron does dissolve, the electrolytic theory is so far satisfactory; if it does not dissolve, we must conclude that the oxygen finds some way of directly attacking the metal.

Almost everyone will admit that in the case of impure iron, with its unhomogeneous physical and chemical constitution, electrolysis will supervene, but it must be remembered that we are now concerned with the underlying cause of the wet oxidation or hydroxylation of iron, regardless of its state of chemical purity.

According to the dissociation theory, even the purest water contains free hydrogen ions to the extent of about 1 grm. in 10,000,000 litres. If iron dissolves in the purest water it should be by interchange with hydrogen, and as Whitney (*loc. cit.*, p. 10) has pointed out, pure water is to this extent an acid. In order to get experimental evidence on this crucial point, Whitney describes the following experiment:—

"A clean bottle was steamed out for a time to remove soluble alkali from the glass, and was then filled with pure distilled water, which was kept boiling by passing steam

These investigators do not believe that hydrogen is evolved during the rusting of iron, or that iron dissolves even to the slightest extent in pure water. They also claim that the electrolytic theory affords no explanation that substances such as chromic acid and potassium bichromate inhibit the rusting of iron. The description of the experiment on which Dunstan based his opposition to the electrolytic theory is quoted verbatim, as follows:—

"A flask of 600 cc. capacity, filled with distilled water, was boiled for fifteen minutes; two pieces of purified iron, each about $1\frac{1}{2}$ inches square, was then placed in the flask, and an indiarubber stopper carrying a glass tube which projected 7 to 8 inches above the stopper and ended in a capillary was fitted into the neck of the flask, the water being kept boiling continuously. The water was allowed to boil for five minutes longer, when the capillary was sealed and the stopper coated with paraffin-wax. This flask was left at the ordinary temperature for three weeks, in the course of which no visible change occurred. It was then opened, when one-half of the liquid was quickly poured into a beaker, the other half being left in contact with the iron in the flask. The liquid in the beaker on exposure to the air showed no cloudiness, no yellow coloration, and no separation of rust. In fact, on testing the liquid for iron by the extremely delicate thiocyanate reaction not a trace could be detected. The pieces of iron

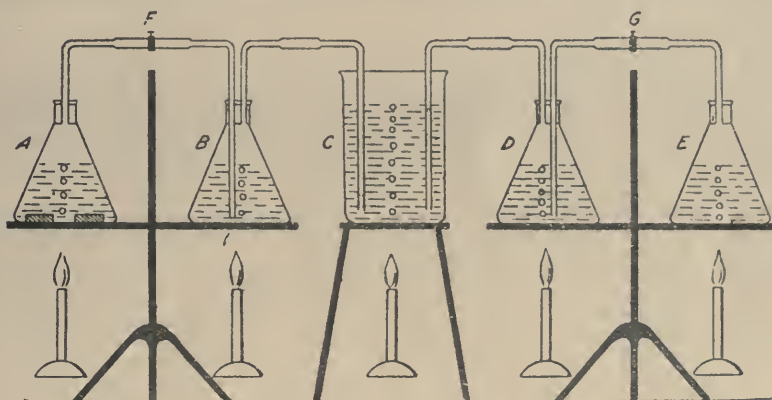


FIG. 2.—APPARATUS USED TO DETERMINE THE EXTENT OF THE SOLUBILITY OF IRON IN PURE WATER.

through it for fifteen minutes. While still boiling, a bright piece of iron was placed in the bottle. A stopper (in some cases rubber and in others cork) carrying a tube open in a capillary several inches above the stopper was inserted into the bottle and firmly fastened in place, the water being kept boiling. Finally, the glass capillary was heated hot by means of a blowpipe, and sealed by squeezing the walls together. The bottle was then allowed to cool to a temperature of about 80°C ., and the neck of the bottle was finally covered with paraffin to prevent leaking. It was thought that in this way the oxygen, carbonic acid, and other gases in the water were completely removed. Bottles containing iron and sealed in this manner have stood without any visible change for weeks. In some cases a little air was subsequently admitted to bottles which had stood in this way with the iron apparently unaffected, and within a few minutes the water became cloudy, and assumed a yellow colour. Ordinary rust rapidly deposited upon the glass and in spots upon the metal. In fifteen or twenty minutes the production of rust throughout the bottle was perfectly evident. It seemed plain from the rapidity of formation of oxide and its precipitation on the glass that the iron had dissolved in the water before the addition of the air, and that the latter simply permitted the formation of the insoluble oxide."

Dunstan and his co-workers reviewed and repeated Whitney's experiment and failed to confirm his result.

in the open flask after an hour showed signs of rusting, just as in ordinary cases, but the phenomena described by Whitney were not observed. We are therefore unable to confirm Whitney's statement that liquid water alone is capable of dissolving even an infinitesimal quantity of iron. This being the case, the theory based on this statement becomes untenable."

It is quite clear that the point at issue is an important one, on which hangs the decision as between the two theories. In order to obtain more light on the subject the writer devised the following experiment, which is sufficiently simple to be repeated by anyone without encountering any difficulties whatever. The apparatus used is shown in Fig. 2.

The two clean Jena glass flasks, A and B, are three-quarters filled with pure freshly distilled water. Two drops of an alcoholic solution of phenolphthalein indicator (1 grm. in 100 cc. pure alcohol) are added to the water in each of the flasks. The beaker C is more capacious than the flasks A and B. The flasks D and E are used in each experiment as blanks to check the results obtained. After connecting up as shown, the water in each vessel is simultaneously boiled very vigorously until about one-quarter is boiled off. The rubber stopper in A is then lifted, and clean polished strips of iron quickly slipped in. The stopper is again tightly inserted, and the boiling continued for about fifteen minutes. The lamps under A and E are then extinguished,

while the water in B, C, and D continues to boil. As soon as flasks A and E have sucked back boiling water so that they are completely filled, the lamps under flasks B and D are also extinguished. When B is quite full, flasks A and E are quickly cooled by surrounding them with cold water. The valve at F is then closed. By this means the bright specimens are immersed in water practically free from air, oxygen, or carbonic acid, and may be kept under observation for any desired length of time. This experiment has been repeated a great number of times with different samples of iron and steel, and no rusting has ever been observed unless air was allowed to enter.

It has been shown that the electrolytic theory of the wet oxidation of iron is based on the premise that iron must first go into solution, an equivalent amount of hydrogen being set free. The resulting ferrous hydroxide in solution betrays its presence by producing a pink coloration with the phenolphthalein indicator. In every experiment made the pink colour was seen, although in some cases the colour developed slowly and only after the lapse of a number of hours. That the colour was not due to the action of the water on the Jena glass was shown by the fact that no colour appeared on the blank side of the experiments.

Another simple experiment was made in order to determine the concentration of hydroxyl ions that must occur before a pink colour can be distinctly seen. 550 cc. of distilled water containing 1 cc. of phenolphthalein indicator was boiled down in a Jena flask to 500 cc. One one-hundredth normal potassium hydroxide solution was then run into the quickly cooled water from a burette. It was thus found that about 1 cc. of one one-hundredth normal potassium hydroxide was the limit of the quantity necessary to produce a distinctly visible pink colour; 1 cc. of one one-hundredth normal potassium hydroxide contains 0.00017 gm. of hydroxyl. This quantity in 500 cc. of water represents a concentration of about 0.35 part of hydroxyl per million. Since the flasks shown in Fig. 2 contain when quite full 360 cc., there must have been present a weight of hydroxyl ions approximately equal to $0.35 \times 360 \times 10^{-6} = 0.00012$ gm. OH. This corresponds to an amount of ferrous iron dissolved equal to $11.2 \times 360 \times 10^{-6} = 0.00040$ gm. Fe.

In referring to Dunstan's experiment it will be seen that he boiled two small pieces of iron $1\frac{1}{2}$ inches square for only five minutes in 600 cc. of water. At the end of the test 300 cc. was poured off to be tested for iron. It is hardly likely under these conditions that, had this experimenter added phenolphthalein to the water, he would have reached the limit of visibility of the pink colour. Granting, however, that he had reached this point, it is apparent that he was making tests for iron in a solution that contained in each centimetre no more than 0.000001 gm. of iron. By carefully evaporating the entire 360 cc. to dryness in a clean platinum dish, with especial precaution to avoid the entrance of dust, the writer has not only been able to show the presence of iron with the ordinary test reagents of ammonium thiocyanate and ferrocyanide, but has also quantitative evidence of the approximate correctness of the amount present, as estimated from the visibility of the colour produced by phenolphthalein.

Six polished strips of iron, $2\frac{1}{2}$ by $\frac{1}{4}$ by $\frac{1}{16}$ inch, were boiled in flask A in the apparatus shown in Fig. 2, as already described. After the water in flask B had sucked back, flask A was allowed to stand until a pink colour was just visible. The contents of the flask were then evaporated to dryness, the phenolphthalein burned off, and the residual ferric oxide weighed. The residue weighed 0.0006 gm., equivalent to 0.0004 gm. of iron.

Since it was thought that some doubt might be felt whether even the small amount of phenolphthalein present could attack the iron, the experiment was repeated with iron and boiled water alone, but the results invariably showed that a small amount of iron had dissolved. In view of the ease with which these experiments can be confirmed it would seem needless to yield more space to this

phase of the discussion. It appears to the writer to be demonstrated that Whitney was right in his assertion that iron goes into solution up to a certain maximum concentration in pure water without the aid of oxygen, carbonic acid, or other reacting substances.

This point established, it becomes apparent that the rusting of iron is primarily due, *not to attack by oxygen, but by hydrogen ions*. Absolute confirmation of this view will be given later on.

Stimulating and Inhibiting Effects of certain Substances upon the Corrosion of Iron.

All substances in solution which contain hydrogen ions, such as acids, stimulate the corrosion of iron. This is also true of salts of strong acids and weak bases, which, though perfectly stable in a dry condition, hydrolyse in solution to an acid reaction; or which, though neutral in fresh solutions, undergo slow decomposition under the action of light, with the formation of acid salts or free acid. With certain exceptions, salts which are perfectly neutral in solution do not prevent oxidation but appear to aid it by increasing the electrolytic action. All substances which develop hydroxyl ions in solution, such as the alkalis or salts of strong bases with weak acids, to a certain extent inhibit, and, if the concentration is high enough, absolutely prohibit the rusting of iron.

Under the electrolytic theory the explanation of the protection afforded by hydroxyl ions is a simple one. Owing to the small dissociation of water, hydrogen ions cannot exist in a solution in which the hydroxyl ions are in excess. As hydrogen ions cannot exist or be locally formed in sufficiently strong alkaline solutions, no attack is made upon the iron, which remains permanently unaltered. If, however, the concentration of the hydroxyl ions is not sufficiently great, electrolysis can go on with an apparent stimulation of the pitting effects similar to that produced by perfectly neutral electrolytes, such as sodium chloride.

As has already been noted, solutions of chromic acid and potassium bichromate inhibit the rusting of iron. In order to determine the concentration necessary to produce complete protection, a number of polished strips of two different samples of steel were immersed in bichromate solutions of increasing concentration, contained in tubes which were left quite open to the air. There were twelve tubes in each series, ranging by regular dilutions from tenth-normal down to ten-thousandth normal. At the end of two months the last four tubes showed graded rusting with accumulation of ferric hydroxide. No rusting had occurred in any of the solutions above tube No. 8, which contained six-hundred-and-fortieth normal bichromate, a strength corresponding to about 8 parts of the salt in 100,000 parts of water, or about 2 pounds to 3000 gallons. Since solutions of bichromate do not hydrolyse with an alkaline reaction, but, on the contrary, are usually slightly acid, some other explanation must be found for this remarkable phenomenon. On first thought it would seem a paradox that a strong oxidising agent should have the effect of preventing the oxidation of iron, and yet this is precisely the case. If, however, the initial cause of rusting is the hydrogen ion, it is possible to believe that under certain conditions oxygen would prove the most effective of all inhibitors. As has been stated, Dunstan, Jowett, and Goulding have claimed that this peculiar action of chromic acid and its salts is due to the fact that they destroy hydrogen peroxide. This explanation is not satisfactory, as has been pointed out, and it is fair to inquire whether the electrolytic theory is capable of furnishing a solution of the problem. Furthermore, it will be shown that additional evidence can be brought forward which cannot be made to apply to any other theory.

The writer has observed that if a rod or strip of bright iron or steel is immersed for a few hours in a strong (5 to 10 per cent) solution of potassium bichromate, and is then removed and thoroughly washed, that a certain change has been produced on the surface of the metal. The surface may be thoroughly washed and wiped with a clean cloth

without disturbing this new surface condition. No visible change has been effected, for the polished surfaces examined under the microscope appear to be untouched. If, however, the polished strips are immersed in water it will be found that rusting is inhibited. An ordinary untreated polished specimen of steel will show rusting in a few minutes when immersed in the ordinary distilled water of the laboratory. Chromated specimens will stand immersion for varying lengths of time before rust appears. In some cases it is a matter of hours, in others of days or even weeks before the inhibiting effect is overcome.

The passivity which iron has acquired can be much more strikingly shown, however, than by the rusting effect produced by air and water. If a piece of polished steel is dipped into a 1 per cent solution of copper sulphate, a ten-second immersion is sufficient to plate it with a distinctly visible coating of copper which cannot be wiped off. A similar polished strip of steel which has been soaked overnight in a concentrated solution of bichromate and subsequently well washed and wiped, will stand from six to ten ten-second immersions in 1 per cent copper sulphate before a permanent coating of copper is deposited. Even a momentary plunging of the metal into the bichromate will induce a certain passivity, but the maximum effect appears to require a more prolonged contact with the solution.

The first explanation of this phenomenon which naturally presents itself is that a thin film of either oxide or chromate has been formed on the surface of the metal. It is almost inconceivable, however if such a film is formed, that it cannot be seen with the aid of a microscope. There is evidence which appears to indicate that no such film of oxide is formed. It is easy to cover polished iron with a visible film of oxide by simply flaming it gently in a Bunsen burner. Such films do not succeed in protecting the iron either from the rusting or the copper sulphate test. Still more convincing than this is the fact that if a polished surface which has been rendered passive by immersion in bichromate is heated to 100° C. for some hours, its passivity disappears and it again behaves in a normal manner. None of the oxides or chromates of iron are in any sense volatile compounds, so that if a solid but invisible film is really formed, it is in some manner dissipated by heat. Further than this, a chromated strip of iron which is kept in a vacuum soon loses its passivity, whereas a similar strip kept under ordinary conditions remains passive for long periods.

The passivity of iron was discovered by Keir in 1790 (*Phil. Trans.*, 1790, p. 359). Since the phenomenon is produced only by strong oxidising agents or by galvanic contact when oxygen can separate on the iron, it was explained by Faraday, Wiederman, and others (*Dammer's Anorg. Chem.*, 1893, iii., 294) as due to a thin oxide film. From the evidence given above, however, it seems that the passivity of iron is better explained as a polarisation effect produced by the separation and retention of oxygen on the surface of the metal. If the rusting of iron is due primarily to the action of hydrogen ions, iron in the condition of an oxygen electrode should be more or less well protected from electrolytic attack.

Keir (*Dammer's Anorg. Chem.*, 1893, iii., 294) observed that polished iron which had been immersed in red fuming nitric acid was altered in some manner so that its power of precipitating silver and copper from their solutions was inhibited, and this occurred, in the discoverer's own words, without the least diminution of metallic splendour or change of colour." In the writer's experience red fuming nitric acid does not produce the passive condition as successfully as solutions of chromic acid and its salts. Mugdan discussed the passivity acquired by iron which was immersed in fuming nitric or sulphuric acids and concluded that it was not due to the formation of an oxide film, but was a true passivity in the sense of an ennobling (*Veredlung*) of the metal (*Zeit. Elektrochemie*, 1903, ix., 454) accompanied by a low electrical potential.

Moody (*loc. cit.*, p. 15) asserts that potassium bichromate prevents the formation of rust, owing to the fact that it slowly dissolves iron and its hydroxides. He observed

that the addition of ammonia to solutions of chromic acid and its salts which had been allowed to act on iron produced precipitates of hydroxide. This point has been carefully investigated by the writer, with the following results:—Iron which is free from manganese is not attacked by solutions of bichromate, even if boiled for days in a flask fitted with a return condenser. Manganese is, however, readily soluble in bichromate solutions, and therefore iron rich in manganese yields a sufficient amount to the solvent action to produce a small amount of brownish manganese hydroxide when the bichromate solution is poured off, made slightly ammoniacal, and allowed to stand. If metallic manganese is boiled in bichromate solutions it dissolves readily, and subsequent addition of ammonia produces an abundant precipitate of brown manganese hydroxide.

If polished iron is allowed to stand for some time in standard tenth-normal potassium bichromate solution, the oxidising strength of the latter as measured by its titration value is slightly reduced without the solution of the iron or the production of any visible effect. Under the same conditions a standard solution of neutral potassium chromate is slightly reduced with the appearance of a small amount of chromic hydroxide. In fact, all the evidence obtainable points to the abstraction by the iron of some of the available oxygen of chromic acid and its salts without the formation or solution of iron oxide films.

In order to show beyond doubt that an oxygen electrode is formed by immersing iron in a strong solution of bichromate the following experiment was made:—Two polished steel electrodes were prepared and chromated by immersion for a number of hours in a strong solution of potassium bichromate. The prepared electrodes were then thrust tightly through a rubber stopper which closed the Jena flask A, which was then filled with pure freshly boiled distilled water in the manner shown in Fig. 1. The electrodes were then attached to the poles of a primary battery at about 2 volts potential. At the end of half an hour, although the potential was not sufficient to disengage bubbles of gas and no visible change had occurred, the electrode which was connected to the zinc pole of the battery had lost its passivity, the other retaining it.

It might still be objected that if a film of oxide had been formed it might suffer reduction at the negative pole. It is, however, very easily shown that electrodes which have been oxidised by gentle heating are not reduced under the conditions of this experiment.

Wood (*Am. Soc. Mech. Eng. Trans.*, 1895, xvi., 671) in 1895 commented on the power of paints and pigments containing certain oxidising agents, notably potassium bichromate and lead chromate, to form on iron and steel surfaces a thin coating of oxide which so effectually protects the metallic surfaces from corrosion that after the removal of the paint the metal still resists atmospheric effects for a long time, as well as the stronger effect of immersion in sea water or acidulated waters and sulphurous and other vapours. This action, Wood adds, is very obscure and not thoroughly understood; but the fact remains, and extended experiments in this field only demonstrate its presence and usefulness.

The oxide film theory has been held for many years to account for the passivity of iron, but in the writer's opinion the protection afforded by certain oxidising agents is electro-chemical and not mechanical.

(To be continued).

Atomic Weight of Silver.—A. Leduc.—Dubreuil has recently calculated the atomic weight of silver to be 107.994 taking $O = 16$, but if $O = 16.027$ the value obtained is 107.81, which is considerably lower than 108. He also states that the result is more likely to be correct the greater the number of methods employed to find it, but it should be observed that this is only true if all the methods are equally good, and it is actually better to rely upon one single method if the others are known to be comparatively inaccurate.—*Comptes Rendus*, cxlvii., No. 21.

PROCEEDINGS OF SOCIETIES

CHEMICAL SOCIETY.

Ordinary Meeting, December 17th, 1908.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

ON the question of admitting women to the Fellowship of the Chemical Society, the PRESIDENT was desired by the Council to make the following statement:—

As already announced, the recent ballot on this question showed that of those among the 2900 Fellows of the Society who voted, 1094 were in favour of, 642 opposed to, the admission of women to the full rights and privileges of Fellowship. Consequent on this difference of opinion three considerations presented themselves.

1. In 1904 the opinion of Counsel was taken as to the eligibility of women for Fellowship under the existing Charter, and your Council was advised that married women are certainly excluded, whilst the position of unmarried women is extremely doubtful, and that it would not be wise to admit women to Fellowship without first applying for a Supplemental Charter. Such a course would involve the Society in considerable expense unless, as has been suggested, the cost were met in part by the petitioners; moreover, your Council was advised on a previous occasion when application for a Supplemental Charter with another object in view was under discussion, that in the opinion of Counsel it was "highly improbable that the Government department before whom the application must come would be disposed to listen to the application unless it represented the practically unanimous vote of the Fellows, and that any active opposition by even a small minority would probably be fatal" (*Proceedings*, 1898, p. 38).

2. Assuming, however, that a successful application for a Supplemental Charter were made, and a certificate of candidature on behalf of a woman were presented, the ballot, if reflecting the above-mentioned figures, would result in the rejection of the candidate, because at least three-fourths of those voting must be in favour.

3. Your Council might accord to women the privilege of using the Library and attending the meetings, and allow them to purchase the publications of the Society at approximately cost price.

After mature deliberation your Council has decided by a considerable majority that it would remove some of the disabilities experienced by women chemists if the following resolution were adopted.

"That in the opinion of this Council it is desirable that, at any time, on recommendation by three Fellows of the Society, women be accepted as Subscribers to the Society. Such women Subscribers shall pay an annual fee of thirty shillings; they shall be admitted to all ordinary meetings of the Society; they shall have the same use of the Library as the Fellows, and they shall be supplied with the *Proceedings*, *Transactions*, and Annual Reports of the Society as these are issued."

This resolution has now been adopted.

It was further announced by the PRESIDENT that the Society was once more indebted to Sir Henry Roscoe for a valuable gift of books, comprising 636 volumes. The meeting endorsed with acclamation the vote of thanks already accorded Sir Henry by the Council.

The seventieth birthday of Professor Dr. G. Lunge will be celebrated on September 15th, 1909, and a local committee has undertaken to arrange a suitable commemoration of the occasion; the PRESIDENT stated that those Fellows who desire to show their sympathy with the festival are requested to communicate with Herrn Dr. E. Berl, Zürich IV., Sonneggstrasse 84.

Mr. M. Barrett was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. George Henry Joseph Adlam, B.A., 86, Southmoor Road, Oxford; Hubert Brunskill, 7, Friarage Gardens, Hartlepool; John Wilberforce Green, 22, Alwyne Road, Wimbledon; John Esson McGillivray, M.A., 15, Regent Street, Hartlepool; William Norton Morley, B.Sc., 325, Brownhill Road, Catford, S.E.; Frederick Hubert Painter, B.Sc., Heatherbank, Alum Chine Road, Bournemouth; Colston James Regan, 14, Penerley Road, Catford, S.E.; James Thomas Stevenson, 67, Surrey Street, Sheffield.

Of the following papers, those marked * were read:—

*266. "*Silicon Researches. Part XI. Silicotetrapyrrole.*" By JAMES EMERSON REYNOLDS.

Much of the work recorded in former papers of this series related to the action of silicon halides on aromatic compounds, including the amino-group, or its equivalent, as a side-chain. It was shown that well-defined, crystallised substances could be formed, such as $\text{Si}(\text{NH}\cdot\text{C}_6\text{H}_5)_4$, in which silicon was obtained for the first time wholly combined with nitrogen. In the course of the study of these substances, it became evident that the inquiry should be carried a stage or two farther, so as to include compounds in which nitrogen forms part of a ring, as in pyrrole and pyridine.

Silicon tetrachloride can be added to pure pyrrole with little effect, but when some light petroleum is poured in, complete mixture is effected and a brown condensation product, containing a small and variable proportion of silicon, separates out. This feeble action of the free base is in strong contrast with the violent interaction of aniline and the silicon compound.

It was found, however, that when potassium pyrrole, $\text{C}_4\text{H}_4\text{NK}$, was treated with silicon chloride at a low temperature, energetic action ensued, potassium chloride and a crystalline substance, in fine needles, which proved to have the composition $\text{Si}(\text{NC}_4\text{H}_4)_4$, being formed. This compound melts at 173° (corr.), but decomposes if heated to a materially higher temperature. Its molecular weight, as determined by the boiling-point method, agrees with the above formula. The substance differs materially from silicophenylamide, more especially in the action of heat on it.

*267. "*Silicon Researches. Part XII. The Action of Silicochloroform on Potassium Pyrrole.*" By JAMES EMERSON REYNOLDS.

As a synthesis of pyridine from pyrrole has been effected by the action of ordinary chloroform on potassium pyrrole, it seemed possible that silicochloroform might yield a silicopyridine, that is, a pyridine ring including SiH instead of one CH group.

Violent action occurs when silicochloroform is added to potassium pyrrole, and the mass becomes dark brown or black, owing to the decomposition of a large proportion of the pyrrole, but nothing definite could be extracted from the residues of several such experiments save some of the tetrapyrrole compound described in Part XI. However, when the materials used were cooled to a very low temperature, the interaction was not so violent, and a small quantity of a dark green liquid was extracted, which did not boil at 210° under a pressure of 50 mm., and decomposed rapidly above that temperature. It proved to consist of $\text{SiH}(\text{NC}_4\text{H}_4)_3$ in a nearly pure condition. When cooled in liquid air, it became a deep bronze-green solid, but rapidly liquefied at the ordinary temperature. It is very easily decomposed in moist air.

Another compound was obtained during the preparation of the tripyrrole derivative; this is a liquid boiling at about $135^\circ/50$ mm., and has the composition $\text{SiH}(\text{NC}_4\text{H}_4)\text{Cl}_2$. It is easily decomposed by water, and fumes in the air. Neither this liquid nor the tripyrrole compound exhibits any characters of a silico-nitrogen-carbon ring, but they

promise to prove useful in further attempts to form such a cyclic combination.

*268. "Silicon Halides and Pyridine, Acetonitrile, &c." Part XIII. By JAMES EMERSON REYNOLDS.

It was inferred from the experience obtained with pyrrole that organic substances, including nitrogen wholly combined with carbon, would react feebly, if at all, with silicon halides. A series of experiments has confirmed this view so far as applies to the compounds used, namely, pyridine, acetonitrile, propionitrile, and benzonitrile.

Pyridine gave with silicon tetrabromide the additive compound $\text{SiBr}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$, and the chloride yielded a similar substance, which latter was also obtained by Harden. Acetonitrile and propionitrile also gave additive compounds of the same order with silicon tetrabromide, and much less easily with the chloride, but benzonitrile did not appear to combine with either.

*269. "The Affinity Values of Tropine and its Derivatives." By VICTOR HERBERT VELEY.

It was shown that tropine, the parent base of the atropine and cocaine alkaloids, has a considerably lower affinity value than piperidine, and it was concluded that the stronger piperidine residue is modified by being conjoined to the weaker pyrrolidine residue if the constitution of this base proposed by Willstätter is correct.

Ecgonine, or tropinecarboxylate, possesses all the properties of an amphoteric electrolyte; its nature is in all probability that of an inner anhydride or betaine.

Anhydroecgonine is a stronger base than ecgonine; the affinity value obtained was approximately equal to that of a benzenoid betaine.

Benzoyllecgonine in dilute solution does not remain in combination with hydrochloric acid; its basic function is, therefore, of the order of caffeine.

Cocaine is a relatively strong base, although weaker than ammonia; the effect produced by the substitution of the carboxylic hydrogen by the methyl group is analogous to that previously observed in the case of glycine.

The affinity value of cocaine was found to be approximately $k_b = 2.5 \times 10^{-7}$, by determining the mass of sodium hydroxide, contained in a hydrolysed borax solution, which was required to upset the equilibrium between a certain mass of cocaine combined with hydrochloric acid as a dissolved salt.

The tropeines, atropine and homatropine, have affinity values greater than $k_b = 1 \times 10^{-7}$; it appeared that when aqueous solutions of their hydrochlorides are heated for some time to their boiling-point, no conversion of the lactonic group into the corresponding hydroxycarboxylic acid takes place.

*270. "Hydroaromatic Ketones. Part I. Synthesis of Trimethylcyclohexenone (isophorone) and some Homologues." By ARTHUR WILLIAM CROSSLEY and CHARLES GILLING.

Further investigation of the trimethylcyclohexenone obtained by the interaction of ethyl malonate and chlorodimethylcyclohexenone (*Proc.*, 1908, xxiv., 130) has proved it to be identical with isophorone.

This method for preparing hydroaromatic ketones has been extended by using substituted malonic esters, but, unfortunately, the yields of the initial condensation products become smaller with increase in the molecular weight of the substituting group. Thus while it has been found possible to prepare dimethylethyl- and dimethylpropyl-cyclohexenones, only traces of a condensation product could be isolated from the interaction of chlorodimethylcyclohexenone and ethyl isopropylmalonate, and the method would not, therefore, appear to be of any practical utility for the preparation of the higher members of the series.

*271. "Note on the Determination of the Rate of Chemical Change by Measurement of the Gases Evolved." By JOHN CANNELL CAIN and FRANK NICOLL.

The authors showed that the criticism of their work on

the rate of decomposition of diazobenzene chloride, advanced by F. E. E. Lamplough in a paper bearing the above title and read before the Society in 1906 (*Proc.*, xxii., 280; compare also *Proc.*, 1908, xxiv., 29), and recently published in full (*Proc. Camb. Phil. Soc.*, 1908, xiv., 580), are invalid for the following reasons:—1. It is definitely stated in their paper (*Trans.*, 1902, lxxxi., 1415) that "the flask usually contained pieces of broken glass for purposes of adjustment, and was well shaken during this operation (of heating the diazo-solution to the required temperature) to avoid overheating," and hence supersaturation was impossible. 2. The whole of the calculated amount of nitrogen was measured; hence none was retained by the solution beyond the minimum quantity (which is within the limits of experimental error) ordinarily dissolved.

Moreover, it was pointed out that Lamplough has overlooked Euler's proof that the reaction is accelerated by colloidal platinum, for in the experiments on the decomposition of hydrogen peroxide the platinum stirrer was coated with wax to guard against any possible action of the platinum, whilst this precaution was omitted in the experiments on diazobenzene chloride. This may well account for the higher value of the constants obtained. Further, Euler has proved by experiment that no supersaturation of the solution with nitrogen takes place in the decomposition of the diazo-solution (*Annalen*, 1902, ccxxv., 295). Finally, the authors expressed the opinion that Lamplough's method of measuring the value of constants which vary enormously with the temperature (being multiplied three to four times for a difference of 10°), by omitting to carry out his experiments with a thermometer in the reacting liquid, and by heating the diazo-solution "one or two degrees higher than (the temperature of) the water-bath," which again would raise the value of the constant found, cannot be regarded as an exact one, and the conclusion was drawn that the author's determinations of the values of the constants in question (in which the temperature was carefully maintained at the correct point) are to be looked upon as being the most accurate yet recorded.

DISCUSSION.

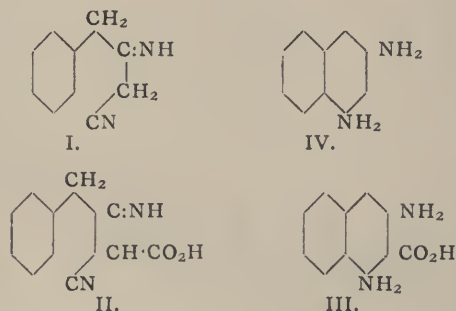
Dr. SENTER said he did not think that Dr. Cain's solution could have been appreciably supersaturated under the conditions of experiment. In his experience, however, solutions in which gases were generated might become highly supersaturated under certain conditions. In the course of an attempt to determine the rate of decomposition of hydrogen peroxide by highly diluted blood (1 of blood to 500 of water) by measuring the oxygen liberated (compare *Zeit. Phys. Chem.*, 1903, xlv., 257), it was found that if the reaction was allowed to proceed quietly for some time, and the bottle was then vigorously shaken, an immediate increase in the volume of the oxygen, amounting to several cc., was observed, although, as shown by subsequent investigation, the course of the reaction is perfectly regular. The amount of oxygen held in solution before shaking amounted at least to five times the ordinary solubility of the gas, and could not be due to chemical combination with the constituents of the blood—(1) because of the exceedingly small proportion of blood present (under ordinary conditions blood only takes up about 20 per cent of its volume of oxygen at atmospheric pressure); (2) because the gas was set free by shaking alone.

The PRESIDENT remarked that certain colloidal and albuminous substances have a considerable influence in causing their solutions to retain gas in solution: he alluded to the solubility of nitrogen in blood-serum. He understood from Dr. Senter that the subject is being investigated by Dr. Findlay.

272. "The Formation and Reactions of Imino-compounds. Part VII. The Formation of 1:3-Naphthylenedianiline from β -Imino- α -cyano- γ -phenylpropane." By STANLEY ROBERT BEST and JOCELYN FIELD THORPE.

In order to study the effect of concentrated sulphuric acid on benzenoid imino-nitriles containing no other sub-

stituting groups in the side-chain, attempts were made to prepare β -imino- α -cyano- γ -phenylpropane (I) by the condensation of phenylacetone with acetonitrile, but without success. It was ultimately found that this substance can be prepared by the action of alcoholic sodium ethoxide on ethyl β -imino- α -cyano- γ -phenylbutyrate, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{NH})\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$, which yields, in the first instance, β -imino- α -cyano- γ -phenylbutyric acid (II.), and subsequently, by the elimination of carbon dioxide, the above imino-nitrile. Both β -imino- α -cyano- γ -phenylbutyric acid and β -imino- α -cyano- γ -phenylpropane pass into naphthalene derivatives on treatment with concentrated sulphuric acid, the former into 1:3-naphthylenediamine-2-carboxylic acid (III.) and the latter into 1:3-naphthylenediamine (IV.) :—



During the experiments on the conditions of hydrolysis of ethyl β -imino- α -cyano- γ -phenylbutyrate with one equivalent of alcoholic potash, it was found that when methyl alcohol is the solvent used the ethyl salt is completely converted into methyl β -imino- α -cyano- γ -phenylbutyrate, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{NH})\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Me}$, and that when water is present the potassium compound of methyl α -cyano- γ -phenylacetoacetate, $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CK}(\text{CN})\cdot\text{CO}_2\text{Me}$, is the sole product. Methyl β -imino- α -cyano- γ -phenylbutyrate passes into methyl 1:3-naphthylenediamine-2-carboxylate on treatment with sulphuric acid.

273. "The Absorption Spectra of Para-benzoquinone, Quinol, and Quinhydrone in the State of Vapour and in Solution." By WALTER NOEL HARTLEY and ALFRED GODFREY GORDON LEONARD.

The absorption spectra of β -benzoquinone and various derivatives in solution were examined by Hartley, Dobbie, and Lauder (*Brit. Assoc. Rep.*, 1902, p. 107), and compared with the various structural formulae which had been proposed for these substances. The chemical reactions of β -benzoquinone were referred to, particularly its powerful oxidising action on alcohols (Ciamician and Silber, *Ber.*, 1901, xxxiv., 1350), and therefore alcohol had been regarded as an unsuitable solvent. Baly and Stewart (*Trans.*, 1906, lxxxix., 506) regard water as an unsatisfactory solvent and employ alcohol. They find the curve for β -benzoquinone in alcoholic solution to be quite different from that observed by Hartley, Dobbie, and Lauder. Experiments made by one of the present authors, in 1902, seemed to show that both alcoholic and aqueous solutions under the action of light yield quinol, and the band of quinol is indicated on the curves. To ascertain the absorption spectrum of pure β -benzoquinone, photographs of the absorption spectrum of its vapour which had been already obtained were compared with those of a solution of the substance in a neutral solvent, such as ether. The results led to an extension of the work to quinol and quinhydrone, in consequence of the discovery of a reversible reaction, expressed in terms of the following equation: $\text{C}_6\text{H}_6\text{O}_2 \rightleftharpoons \text{C}_6\text{H}_6\text{O}_2 + \text{H}_2$, when quinol vapour is heated in air to 147° at atmospheric pressures and exposed to light. When heated in hydrogen, the quantity of β -benzoquinone produced is diminished. Among the conclusions arrived at are, that ether is the only suitable solvent at all concentrations, and that under

the influence of sunlight, or ultra-violet rays, an interaction occurs between the solvent alcohol and the solute β -benzoquinone which leads to the reduction of the latter to quinol or quinhydrone.

274. "The Constitution of Para-benzoquinone." By WALTER NOEL HARTLEY.

In a previous paper the author has shown how the formula for benzene as proposed by Kekulé might be reconciled with those of Armstrong and von Baeyer (*Trans.*, 1905, lxxxvii., 1823). From the evidence obtained during the investigation of β -benzoquinone, and of benzene and its homologues in a state of vapour (*Phil. Trans.*, 1908, A, ccviii., 475), it now appears certain that neither β -benzoquinone nor quinol has a fixed and settled constitution in the strict sense of their usual symbolic representations, or the interpretations of them. It has been proved that β -benzoquinone is a benzene derivative, and furthermore, that it is possessed of a dual character in the sense that the function of the molecule can be either that of a double ketone or of a peroxide, according to circumstances. The reversible reaction described in the previous paper by Mr. Leonard and the author is now under further investigation.

275. "Benzyl Sulphoxide: A Possible Example of Dynamic Isomerism." By JOHN ARMSTRONG SMYTHE.

By the action of hydrochloric acid on benzyl sulphoxide, four to six of the following compounds are produced: benzaldehyde, benzyl chloride, benzyl mercaptan, benzyl disulphide, benzyl sulphide, benzyl disulphoxide, and benzaldehyde benzyl-mercaptale. The study of this reaction under different conditions has shown that it is influenced by temperature and the nature of the solvent in which it takes place; the oxygen of the sulphoxide passes over chiefly into the disulphoxide in aqueous solvents, but progressively larger amounts of benzaldehyde are formed as the solvent becomes more anhydrous and the temperature rises.

To account for these and allied phenomena, it is assumed that benzyl sulphoxide exists in solution in two forms, which differ constitutionally in the position of the oxygen atom in the molecule. On the basis of this hypothesis, a series of equations involving the tautomeric forms is proposed, which gives a simple and consistent account of the formation of all the various products, and enables the hypothesis to be tested by comparison of the quantities calculated from the equations with those found experimentally. The agreement of calculated with experimental results is held to justify the hypothesis.

The quantitative data enable further the equilibrium between the tautomeres under certain conditions to be investigated, and they also show the influence of water as catalyst in the conversion of one form into the other.

Confirmatory evidence of these views is obtained from other reactions of benzyl sulphoxide.

276. "The Chemical Dynamics of the Reactions between Sodium Thiosulphate and Organic Halogen Compounds. Part III." By ARTHUR SLATOR and DOUGLAS FRANK TWISS.

The velocities of the reactions between sodium thiosulphate and the following halogen compounds have been measured: propyl iodide, isopropyl iodide, allyl iodide, chloroacetone, chloroacetophenone, benzyl chloride, *o*-, *p*-, and *m*-nitrobenzyl chlorides, ethyl α -bromopropionate, and ethyl α -bromobutyrate. The great activity of the acetone derivatives is remarkable. Allyl iodide is more reactive than methyl iodide. The activity of the benzyl chlorides is of the same order of magnitude as that of methyl chloride. The *iso*-compounds are less reactive than the corresponding normal compounds.

To explain to a certain extent the results of this and other investigations, it is suggested that the halides exist in more than one form in solution, and that some reagents react with one form and some with another.

277. "Note on the Optical Rotatory Power of Menthyl Cinnamate." By THOMAS PERCY HILDITCH.

The author's observations on menthyl cinnamate (*Trans.*,

1908, xciii., 1) showed that his specimen of this ester, although identical in most physical properties with those described by Tschugaeff (*Journ. Russ. Phys. Chem. Soc.*, 1902, xxxiv., 606) and Cohen and Whiteley (*Trans.*, 1901, lxxix., 1308), possessed in chloroform solution a widely different rotation from that given by Tschugaeff for the liquid ester ($[\alpha]_D -86.65^\circ$).

An opportunity for further investigation of this point has been afforded by experiments made primarily with the view of ascertaining the degree of accuracy of a polarimeter in the University of Jena; two samples of menthyl cinnamate were prepared, one from cinnamic acid procured from Kahlbaum, and the other from acid prepared by the author from benzaldehyde by Perkin's reaction. The menthol possessed a specific rotation $[\alpha]_D^{15} -48.84^\circ$ in 5 per cent chloroform solution. The purification of the esters was accomplished, as previously, by two successive distillations in a vacuum; the boiling-point of each sample was $210-212^\circ/20$ mm.

In 10 per cent chloroform solution the first preparation had $[\alpha]_D^{15} -60.44^\circ$, and the second $[\alpha]_D^{15} -60.50^\circ$; the value previously obtained with menthol, $[\alpha]_D^{20} -48.40^\circ$, was $[\alpha]_D^{20} -60.00^\circ$. On examining the compound without a solvent, however, the observed optical activity was $[\alpha]_D^{15} -85.95^\circ$.

It was obviously a matter of great difficulty to determine, at the temperature of the experiments, the molecular condition of the ester, either undissolved or dissolved in chloroform. The rotatory power in glacial acetic acid was therefore measured, when a 5 per cent solution gave $[\alpha]_D^{15} -60.02^\circ$. It may thus be assumed that the molecular state of the substance here is the same as in chloroform. A molecular-weight determination by the freezing-point method in glacial acetic acid solution showed the ester to be unimolecular (0.2204 ester in 26.804 acetic acid gave $\Delta = 0.113^\circ$, whence $M.W. = 280.8$. $C_{19}H_{26}O_2 = 286$); hence the substance is unimolecular in acetic acid and also in chloroform solution, whilst in the undissolved state it is probably associated. It may be noted that the corresponding menthyl β -phenylpropionate possesses the same rotatory power in the fused state as in chloroform solution.

Similar irregularities have been mentioned by Rupe (*Annalen*, 1903, cccxxvii., 164) in the case of menthyl acetate, which possesses less activity in alcohol solution than when no solvent is used, although all the other menthyl fatty acid esters show greater optical activity in alcohol than in the absence of solvent, and by Freundler (*Comptes Rendus*, 1893, cxvii., 556; *Ann. Chim. Phys.*, 1895, [vii.], iv., 244), who showed that ethyl alcohol, methyl alcohol, and acetone solutions of dipropyl diacetyl-tartrate have a weaker rotatory power than the undissolved substance, whilst dipropyl dibutyl- and dihexyl-tartrates possess stronger activity in these solvents than in the undissolved state.

It follows from the above results that such esters are not in the same molecular condition when undissolved as when in solution, and that any measurements designed for the purpose of comparing the rotatory powers of a series of substances should be conducted in circumstances which ensure that the compounds in question are present in a normal, or, in other words, unimolecular, condition.

278. "Liberation of Iodine from Hydriodic Acid by certain Halogenated Malonyl Derivatives." By MARTHA ANNIE WHITELEY.

During the continuation of the work on derivatives of malonamide (*Proc.*, 1904, xx., 92) and of barbituric acid (*Trans.*, 1907, xci., 1330), it has been observed that the mono- and dibromo-derivatives of these series, compounds containing the complex $-\text{CO}\cdot\text{CHBr}\cdot\text{CO}-$ or $-\text{CO}\cdot\text{CBr}_2\cdot\text{CO}-$, liberate iodine from hydriodic acid at the ordinary temperature according to the equation $>\text{CBr}_2 + 4\text{HI} = >\text{CH}_2 + 2\text{HBr} + 2\text{I}_2$.

In most cases the reaction is complete, and can be employed as a method for estimating the bromine in the compounds. Quantitative results have been ob-

tained with dibromomalonomide, bromomalonyldiurethane, $(\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et})_2\text{CHBr}$, m. p. 148° , 5:5-dibromo-1:3-diphenylbarbituric acid, 5-bromo-5-benzoyl-1:3-diphenylbarbituric acid, $\text{C}_{23}\text{H}_{15}\text{O}_4\text{N}_2\text{Br}$, m. p. 186° , 5-bromo-1:3-diphenyl-2-thiobarbituric acid, $\text{CS}\langle\text{NPh}\cdot\text{CO}\rangle\text{CHBr}$, m. p. 220° , and 5:5-dibromo-1:3-diphenyl-2-thiobarbituric acid, $\text{CS}\langle\text{NPh}\cdot\text{CO}\rangle\text{CBr}_2$, m. p. 190° ; and some of these compounds react also with silver nitrate in the presence of dilute nitric acid, forming silver bromide.

Dichloromalonomide slowly liberates iodine from hydriodic acid at the ordinary temperature, but the reaction is not complete even at 100° .

The replaceability of halogen by hydrogen by the action of hydriodic acid at the ordinary temperature has hitherto been regarded as a characteristic reaction of compounds containing the nitrogen-halogen as distinguished from those containing the carbon-halogen linking (Chattaway, *Trans.*, 1905, lxxxvii., 145; *CHEMICAL NEWS*, 1908, xcvi., 285); since the results quoted above show that this generalisation is no longer tenable, it seemed advisable to publish this preliminary statement. The investigation is being extended to other compounds containing the $>\text{CHX}$ or $<\text{CX}_2$ group to ascertain to what extent the replaceability of the halogen is influenced by the nature of the neighbouring groups.

FARADAY SOCIETY.

Ordinary Meeting, December 15th, 1908.

Dr. T. M. LOWRY in the Chair.

DR. F. J. BRISLEE communicated a paper, which was read by Dr. N. T. M. WILSMORE, on "A Re-determination of the Electrolytic Potentials of Silver and Thallium."

The electrolytic potentials of silver and thallium were re-determined over a range of concentrations and in solutions of two different salts—silver in silver nitrate and acetate solutions, thallium in thallous nitrate and chloride solutions. The measurements were made with a Clark-Fisher potentiometer, employing a Weston cadmium cell as standard and the decinormal calomel electrode as comparison electrode, the liquid potential at the junction of the two being eliminated by a saturated solution of ammonium nitrate. The ionic concentrations were calculated from the most recent conductivity measurements. All measurements were made at room temperature, viz., 17°C . The results obtained for the electrolytic potentials of silver were:—

Silver in silver nitrate: $+1.076 \pm 0.0005$ volt, mean of six determinations.

Silver in silver acetate: $+1.075 \pm 0.0013$ volt, mean of six determinations.

General mean of both series of measurements is: $+1.0757 \pm 0.0006$ volt.

For thallium the results obtained were:—

Thallium in thallous nitrate: -0.042 ± 0.001 volt, mean of six determinations.

Thallium in thallous chloride: -0.042 ± 0.0004 volt, mean of four determinations.

The general mean is: -0.0425 ± 0.0005 volt.

Prof. R. ABEGG (communicated) expressed the hope that English writers would use the symbols proposed by the "Potential Committee" of the German Bunsen Society, and adopted by the Fifth International Congress of Applied Chemistry, when publishing electrochemical work.

A paper entitled "The Heats of Combustion of Aluminium, Calcium, and Magnesium" was read by Mr. FRANK E. WESTON, B.Sc., and Mr. H. RUSSELL ELLIS, B.Sc.

The values given for the heats of formation of Al_2O_3 , CaO , and MgO by various investigators differ very considerably. The authors have investigated the reduction of

the oxides of Al, Ca, and Mg respectively by each of the metals Mg, Ca, and Al. From the theory of the greatest heat development the oxide with lowest heat formation should be reduced by the metals of the other two oxides, and so on. The experiments were carried out under similar conditions, as far as possible, and quantities of from 20 grms. to 50 grms. of the mixture used in all cases. The mixtures were made in the following proportions:—
(1) $\text{Al}_2\text{O}_3 + 4\text{Al}$; (2) $2\text{Al} + 3\text{CaO}$; (3) $2\text{Al} + 3\text{MgO}$; (4) $3\text{Ca} + \text{Al}_2\text{O}_3$; (5) $\text{Ca} + \text{MgO}$; (6) $\text{Mg} + \text{CaO}$; (7) $3\text{Mg} + \text{Al}_2\text{O}_3$. It was found that—

- Mg reduces Al_2O_3 —product contained 7.43 per cent N as nitride, 0.71 per cent Al, and 3.87 per cent Mg.
- Ca reduces Al_2O_3 —product contained 8 per cent free Al.
- Mg easily reduced CaO—product contained 33.65 per cent Ca_3N_2 , 1.29 per cent Ca, and 0.47 per cent Mg.
- MgO is not reduced by Al even at a temperature of 1100°C .
- MgO is slowly reduced by Ca—product contained 5.79 per cent N as nitride, 4.16 per cent Ca, and 0.58 per cent Mg.
- CaO is partially reduced by Al—product contained 8.3 per cent Ca, 6.1 per cent Al, 0.375 per cent N as nitride.

The authors conclude that the heat of combustion of Mg is greater than that of Ca, and Ca than that of Al. However, the heat of combustion of Mg is not much greater than that of Ca. The partial reduction of CaO by Al and of MgO by Ca are probably endothermic reactions, similar to the reduction of B_2O_3 by K and Na. The authors are of opinion that the reactions described above are complicated by the interaction of the hot metals with the air, and in order to throw light on this point experiments are being carried out *in vacuo*.

Dr. H. BORNS said that the question of heats of formation could hardly be discussed until the results of experiments to be made *in vacuo* were known.

Mr. H. K. PICARD was able to confirm most of the results obtained by the authors. He suggested the reaction between alumina and aluminium sulphate as an interesting one to study, as it might prove to be a source of aluminium.

Mr. H. R. ELLIS adduced reasons for supposing that when magnesium was employed the nitride obtained was not, as had been suggested, magnesium nitride, but the nitride of the metal reduced.

Dr. N. T. M. WILSMORE thought the reactions were too complicated to allow of deductions from the heats of formation of simple oxides.

Mr. H. RUSSELL ELLIS, B.Sc., then read a paper on "The Formation of Graphite by the Interaction of Magnesium Powder and Carbonates." (See CHEMICAL NEWS, vol. xcvihi., p. 309).

A preliminary communication on "Colloidal Barium Sulphate" was made by Dr. ERNEST FEILMANN. (See CHEMICAL NEWS, vol. xcvihi., p. 310).

Dr. V. H. VELEY (communicated) suggested many further lines of investigation, such as the use of other colloidal menstrua, the determination of the size of the particles, the conditions of precipitation by acids, and resolution by alkalis, and so on. It appeared possible that every variety, from well-defined crystals to amorphous masses of barium sulphate, could be obtained.

Prof. W. W. HALDANE GEE (communicated) agreed with the author that here was a case of barium sulphate nuclei protected by an organic colloid, and thus producing stable colloidal solutions, in accordance with Quincke's observations, that if there are three immiscible liquids, A, B, and C, B will tend to form a layer separating the other two if $T_{AB} + T_{BC} < T_{AC}$, T being the respective surface tensions. The coating might form an electric "double layer," preventing neutralisation of the nucleus by

oppositely-charged ions. He suggested further extensions of the method.

Dr. G. SENTER thought examination of the particles by the ultra-microscope would prove instructive.

Dr. H. BORNS suggested a possible application of these colloidal solutions in the production of uniform reflecting surfaces—for photometric purposes, for example.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

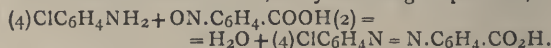
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvii., No. 21, November 23, 1908.

Borotungstic Acids.—H. COPAUX.—When one part of neutral sodium tungstate and one and a-half parts of boric acid are treated with boiling water, part of the sodium of the tungstate is fixed by the boric acid, and the free tungstic acid forms a mixture of sodium metatungstate and borotungstate, the concentration of the latter being greater the more boric acid there is in the liquid. When the solution is allowed to stand a crystalline mass of boric acid and sodium polyborates separates, and from the liquid after concentration with the addition of some boric acid two borotungstic acids can be isolated. One crystallises in the hexagonal system, and has the formula $\text{B}_2\text{O}_3 \cdot 28\text{WO}_3 \cdot 62\text{H}_2\text{O}$, and the other forms quadratic crystals and its formula is $\text{B}_2\text{O}_3 \cdot 24\text{WO}_3 \cdot 66\text{H}_2\text{O}$. The heptametatungstic acid is hexabasic, and is only fairly stable. The hexametatungstic acid is rather more soluble and much more stable; it is isomorphous with silicotungstic acid, and the double formula of the latter corresponds with that of the boron acid, except as regards water of constitution.

Action of Antimony Trichloride on Nickel. Formation of NiSb .—Em. VIGOUROUX.—The action of vapours of antimony trichloride on powdered nickel at 600° leads to the formation of a compound of formula NiSb . It is a metallic crystalline powder, reddish violet in colour, and non-magnetic. It fuses when heated to 1100° , and begins to decompose at 1400° , giving up antimony. It is attacked by chlorine and oxygen at a red heat. Sulphur decomposes it before the melting-point is reached. Hydrochloric acid has no effect, even when concentrated, nor dilute sulphuric acid. Concentrated sulphuric acid acts rapidly upon it, and also concentrated nitric acid, especially when the temperature is raised. Fusion with alkalis seems to have very little effect.

Preparation of Azo-o-Carboxylic Acids.—P. FREUNDLICH and M. SEVESTRE.—A good yield of azo-o-carboxylic acids can be obtained by allowing primary aromatic amines to react with o-nitroso acids. Thus, o-nitrosobenzoic acid and p-chloraniline give p-chlorobenzenazo-o-benzoic acid, the yield being 60 per cent,—



In order to prepare the o-nitroso-compounds necessary for this condensation, it is best to apply Baeyer's method for the conversion of aniline into nitroso-benzene; *i.e.*, the oxidation of the amino acids by means of Caro's reagent. This method gives a perfectly pure product free from nitro derivatives.

Theory of Preparation of Monomethylamine by Solutions of Brominated Acetamide.—Maurice FRANÇOIS.—Hofmann supposed that the action of potash on brominated acetamide at 70° takes place in two stages, methyl cyanate being first produced with loss of HBr, and is then converted into methylamine by potash. $\text{CH}_3\text{—CO—NHBBr} + \text{KOH} = \text{KBr} + \text{CO}_2 + \text{CH}_3 + \text{NH}_2$. The

author's experiments, however, show that in the solutions of brominated acetamide used for the preparation of monomethylamine for every molecule of acetamide one molecule of hypobromous acid exists. The bromine is present only as hypobromous acid and in the free state. When such solutions are heated in presence of a concentrated alkali, monomethylamine is formed as the result of a simple oxidation by hypobromous acid in certain conditions of temperature and alkalinity. Monomethylamine can readily be prepared by the action of potassium hypobromite on acetamide.

Humic Matter in Coal.—O. Boudouard.—The oxidation of coal in the air gives rise to brown products of an acid character, soluble in alkalis, and resembling humic compounds. There seems to be a certain relation between the coking power of the coal and the proportion of these substances present. The author has treated coals of various origins with potash in order to extract the humic matter, which he has subjected to an elementary analysis. In the original paper the results are given of fourteen analyses in which the carbon varies from 52 to 67 per cent, the hydrogen from 3 to 5 per cent, and the oxygen from 30 to 44 per cent. When the results of the analyses are examined it is found that they fall into four groups, the formulæ of the humic matter being $C_{18}H_{14}O_6$, $C_{18}H_{18}O_9$, $C_{18}H_{14}O_9$, $C_{18}H_{14}O_{11}$ respectively.

No. 22, November 30, 1908.

Chlorides and Oxychlorides of Thorium.—Ed. Chauvenet.—The anhydrous chloride of thorium, $ThCl_4$, can be prepared conveniently by the action of phosgene gas on the oxide at a red heat. $ThO_2 + 2COCl_2 = 2CO_2 + ThCl_4$. The current of gas must be very slow so that the anhydrous chloride may sublime by degrees in the front of the tube in which the oxide is heated. The author finds that though this compound has been described as not deliquescent it combines fairly rapidly with the water vapour of the atmosphere. When an aqueous solution of the anhydrous chloride is evaporated on the water-bath and then in a dry atmosphere to constant weight, the hydrated chloride, $ThCl_4 \cdot 7H_2O$, is obtained. Heating to $120-160^\circ$, again to constant weight, gives the oxychloride, $Th(OH)Cl_3 \cdot H_2O$. At about 200° , $ThCl_4 \cdot 7H_2O$ is transformed into a compound intermediate between $ThOCl_2$ and $ThOHCl_3$, and at 250° in a current of hydrogen chloride gas the hydrated chloride loses half its chlorine and gives the anhydrous compound $ThOCl_2$.

Action of Antimony Trichloride on Cobalt and its Alloys with Antimony.—F. Ducelliez.—Powdered cobalt decomposes antimony trichloride at 700° , at 800° the compound $CoSb$ being formed. The alloys of cobalt and antimony can be divided into three classes:—1. Those containing less than 67.04 per cent of antimony. These give crystals of $CoSb$ when treated with hydrochloric or sulphuric acid. 2. Those containing from 67.04 to 80.27 per cent of antimony. These are readily decomposed on heating, and give the compound $CoSb$ when kept at 1200° in a current of hydrogen. 3. Those containing more than 80.27 per cent of antimony. These yield the antimonide, $CoSb_2$, when treated with nitric and hydrochloric acids. The two substances $CoSb$ and $CoSb_2$ are the only compounds which exist among the alloys of cobalt and antimony. Chemical reagents have similar effects on the two compounds, e.g., when heated in chlorine heat is disengaged and antimony trichloride distils. With oxygen incandescence is observed, and antimony oxide is formed. Sulphur attacks them violently. Dilute or concentrated nitric acid dissolves the cobalt, and leaves a deposit of antimonious anhydride. Aqua regia entirely dissolves them, but alkalis and alkaline carbonates when fused with them attack them only with difficulty.

Uranium Disilicide, Si_2Ur .—Ed. Defacqz.—By the aluminothermic method, which may be applied to the oxides of tungsten and molybdenum to prepare the silicides from them, uranium silicide Si_2Ur can be prepared.

It is a grey metallic powder of density 8 at 0° . Chlorine decomposes it at 500° giving the corresponding chlorides. It is soluble in hydrofluoric acid, insoluble in nitric acid, hydrochloric acid, sulphuric acid, and aqua regia. It is not readily oxidised, and is unaltered in air even at a red heat. Mixtures of alkaline nitrate and carbonate attack it only slightly at their melting-point, but at a red heat fused alkalis and alkaline carbonates convert it into alkaline silicate and uranate. Potassium bisulphate acts on it slowly at temperatures above its melting-point.

Hydrogenation of Triphenylmethane. Tricyclohexylmethane.—Marcel Godchot.—Triphenylmethane can be hydrogenated by leading its vapour over a catalysing metal at a suitable temperature by means of a current of hydrogen. The product of hydrogenation is tricyclohexylmethane, $(C_6H_{11})_3CH$. It is a colourless liquid with an aromatic smell. It boils at 140° under 20 mm., and its density at 18° is 0.8406. It is insoluble in water, slightly soluble in alcohol and acetic acid, dissolves readily in ordinary ether and benzene. Its solutions are not fluorescent. It gives a brown coloration with hot concentrated sulphuric acid, and with bromine yields a brominated derivative.

No. 23, December 7, 1908.

This number contains no chemical matter.

Berichte der Deutschen Chemischen Gesellschaft.

Vol. xli, No. 16, 1908.

Methyl and Ethyl Ester of Thiophosphoric Acid.—P. Pitschmuka.—When phosphorus sulphochloride acts on alcohols the chloranhydride of the corresponding acid is obtained, $SPCl_3 + R(OH) = HCl + SPCl_2(OR)$. The acid chlorides are colourless liquids which cannot be distilled at ordinary pressures, and which are not decomposed by alcohols and water. With sodium alcoholate they give neutral esters of thiophosphoric acid. By the action of $PSCl_3$ on solutions of sodium alcoholate in methyl and ethyl alcohol, the esters $SP(OCH_3)_3$ and $SP(OC_2H_5)_3$ were obtained. They readily form complex compounds, e.g., $SP(OCH_3)_3 \cdot 2HgCl_2$, $3SP(OCH_3)_3 \cdot 2FeCl_3$, $PSO(HgCl)(OC_2H_5)_2 \cdot HgCl_2$, which possess an interesting property. Thus, on heating $SP(OCH_3)_3 \cdot 2HgCl_2$ to 103° , it gives up two molecules of $HgCl_2$, and a salt-like substance remains behind,—

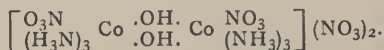


A similar compound, $PSO_3CH_3(TlCl_2)_2$, is obtained with thallium chloride. The methyl ester reacts at the ordinary temperature with sodium methylate, yielding the salt $PSO_3Na(OCH_3)_2$, from which the compound $PSO_3Ag(OCH_3)_2$ can be prepared by the addition of silver nitrate. This same compound is obtained by mixing an alcoholic or ethereal solution of silver nitrate with the methyl ester, the other product of the reaction being methyl nitrate, $SP(OCH_3)_3 + AgNO_3 = PSO_3Ag(OCH_3)_2 + CH_3 \cdot NO_3$. Similar reactions occur between silver nitrate and the ethyl ester, and the ester and sodium ethylate. In the compound $PSO_3Ag(OCH_3)_2$ the metal can be bound to the phosphorus either by means of oxygen or by means of sulphur; since, by converting the compound into esters, thiophosphoric acid derivatives are obtained, there can be no doubt that the constitution is represented by the formula $OP(SAg)(OCH_3)_2$.

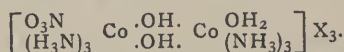
Indicator suitable for Use with Hundredth-normal Alkali Solution.—E. Rupp and R. Loose.—The authors have found that a compound, to which they have given the name methyl-red, is exceedingly sensitive towards alkalis, surpassing hæmatoxylin; it may be used in place of iodoeosin. It is pale yellow in alkaline and neutral solution and red-violet in acids. It is prepared by dissolving amidobenzoic acid in alcohol, adding concentrated hydrochloric acid, diazotising with sodium nitrite, and adding freshly distilled dimethyl aniline. The mixture is then

heated for half-an-hour on the water-bath, the compound is separated off from the solution, treated with hot glacial acetic acid, and water is added to the boiling liquid till a turbidity is produced. On cooling, the methyl-red separates out in glittering violet needles. A 2 per cent alcoholic solution is used for the indicator. The compound appears to be an azo-compound of *o*-amidobenzoic acid and dimethylaniline.

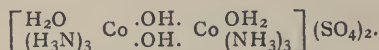
Conversion of Hexamminetrioldicobaltic Salts into Octamminedioldicobaltic Salts.—A. Werner. — By treating hexamminediold sulphate with semi-dilute nitric acid a dinitrato-nitrate is formed:—



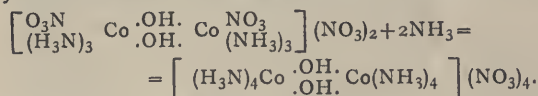
This salt is hydrated very rapidly in aqueous solution, and then reagents precipitate salts of the nitratoaquo-hexamminedioldicobaltic series:—



The first nitrate does not belong to the latter series, for in aqueous solution it has a neutral reaction, while the salts of the aquo series, like all aquocobaltic salts, are acids. When the aqueous solution of the nitrate is allowed to stand for a long time on addition of a soluble sulphate, difficultly soluble diaquo-hexamminedioldicobaltic sulphate separates:—



The dinitrato-hexamminedioldicobaltic nitrate takes up two molecules of NH_3 in liquid ammonia, and gives a good yield of octamminedioldicobaltic nitrate:—

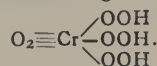


The octamminediold-salt was obtained pure in the form of bromide.

Decammine- μ -amino-dicobaltic Salts.—A. Werner. —Octammine- μ -amino-ol-dicobaltic nitrate gives with nitric acid a nitrato-aquo-compound, which is converted into decammine- μ -aminodicobaltic nitrate in liquid ammonia. From the nitrate other salts of the same series can be obtained. They all crystallise well, and are red in colour. The constitutional formula appears to be $\text{Cl}_2[(\text{H}_3\text{N})_5\text{Co}-\text{NH}_2 \dots \text{Co}(\text{NH}_3)_5]\text{Cl}_3$. These decammine salts show a remarkable resemblance in colour, and the way in which they separate from their solutions to the rhodochromium salts, $\left[\text{Cr}_2 \begin{array}{c} (\text{NH}_3)_{10} \\ \text{OH} \end{array} \right] \text{X}_5$.

Perchromates.—E. H. Riesenfeld. —The higher oxidation products of chromium can be divided into two classes:—(1) Chromium tetroxide derivatives, (2) the perchromates proper, which include the salts of perchromic acid HCrO_5 (chromium pentaperacid), "blue perchromates," and the salts of perchromic acid H_3CrO_8 (chromium octoperacid), "red perchromates." The determination of the molecular weight of red potassium and ammonium perchromates shows that they are monomolecular, and probably the free acid also has the simple molecular weight. By determining the electro-chemical equivalent of chromium in the red perchromates, it was shown that the chromium was not hexavalent, and an argument against the hexavalency of chromium in the perchromates is provided by the fact that as long as potassium is taken to be mono- and oxygen divalent constitutional formulæ of the perchromates can only be constructed on the assumption that chromium has an odd valency. The comparison of the peroxide of chromium with those of the other elements shows that the oxygen is not electro-chemically monovalent; chromium peroxide is an antozonide like the peroxides of the alkalis and alkaline earths. From experiments on the action of

perchromate on permanganate it appears that both in the red and blue perchromates chromium is heptavalent, the formula of the octoperacid being—



Bismuth Carbonates and Oxalates.—L. Vanino and Emilie Zumbusch. —From a bismuth mannite solution potassium and ammonium carbonate precipitate a carbonate of formula $\text{BiO} \cdot \text{CO}_3 \cdot \text{BiO}$. When a clear concentrated solution of bismuth nitrate is poured into excess of sodium carbonate solution, a precipitate is obtained of composition $5\text{Bi}_2\text{O}_3 \cdot \text{Bi}_2(\text{CO}_3)_3$ if washing is continued till all traces of nitric acid have been removed. If the precipitate is not so thoroughly washed the results of the analysis point to the formula $\text{BiO} \cdot \text{CO}_3 \cdot \text{BiO}$. A precipitate of oxalate is obtained when oxalic acid solution is added to bismuth mannite solution. The formula of the oxalate precipitate is $\text{Bi}_2(\text{C}_2\text{O}_4)_3$ or $\text{Bi} \begin{array}{c} \text{—OH} \\ \text{—C}_2\text{O}_4 \end{array}$, according to the experimental conditions, both salts being very sensitive towards water.

MISCELLANEOUS.

American Philosophical Society. — General Meeting, April 22–24, 1909. —The American Philosophical Society has satisfactorily shown that the interests of useful knowledge in the United States are greatly promoted by the annual General Meetings of the Society. These meetings have proved attractive to its members in all parts of the country, not only because of the general interest in the scientific communications offered, but also because of the opportunities afforded of renewing and extending acquaintanceship among workers in the various fields of knowledge, and they have markedly broadened the field of usefulness of this the oldest scientific Society in America. The General Meeting of 1909 will be held at Philadelphia on April 22nd to 24th, beginning at 2 p.m. on Thursday, April 22nd. The evening of Friday, April 23rd, will be devoted to addresses in commemoration of the centenary of the birth of Charles Darwin and the fiftieth anniversary of the publication of "Origin of Species." Members desiring to present papers, either for themselves or others, are requested to send to the Secretaries, at as early a date as practicable, and not later than March 24, 1909, the titles of these papers, so that they may be announced on the programme which will be issued immediately thereafter, and which will give in detail the arrangements for the meeting. Papers in any department of research come within the scope of the Society, which, as its name indicates, embraces the whole field of useful knowledge. The Publication Committee, under the rules of the Society, will arrange for the immediate publication of the papers presented. The activity of the Society is reflected in the increasing volume of its publications, which constitute a series covering one hundred and forty years, and include *Transactions* in quarto and *Proceedings* in octavo form; its exchange list embraces most of the scientific societies of the world. The Society thus offers valuable avenues of prompt publication and wide circulation of the papers read before it.

MEETINGS FOR THE WEEK.

WEDNESDAY 13th. —Royal Society of Arts, 5. (Juvenile Lecture). "Digging for Ancient Art Treasures," by Chas. Waldstein.
Society of Public Analysts, 8. "Analysis of Complex Candle Mixtures" and "Detection and Estimation of Mercury in Nitro-explosives," by O. Hehner.

THE CHEMICAL NEWS.

Vol XCIX., No. 2564.

TANTALUM, NIOBIUM, AND TITANIUM:

OBSERVATIONS ON.

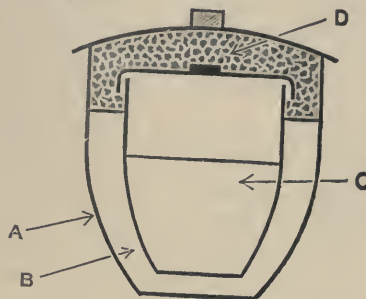
PART II.—ON THE OPENING-UP OF MINERALS CONTAINING THESE BODIES.

By W. B. GILES, F.I.C.

(Continued from p. 4).

In smaller quantities I obtained tantalites and columbites from Finland, Sweden, Norway, Bavaria, Dakota, New Hampshire, Alabama, and other localities. It is curious that none of these minerals exhibit any sign of magnetic properties. When brought near to the poles of a powerful electro-magnetic they are not at all affected, even in a state of fine powder, while many titanium compounds, such as ilmenite, are, as is well known, decidedly attracted. The minerals were first broken up into coarse pieces in a small stone-breaker; it was then seen, especially in the case of the Middleton columbite, that though the lumps of the material appeared to be very free from foreign matter, when they were crushed they disclosed thin inclusions of mica and other silicates. These were picked out as much as possible, and the minerals were then ground so that they would pass a 100-mesh sieve. Several kilograms. of columbite and tantalite were prepared in this manner so as to form standards. In my first trials to remove the tin (which is so troublesome to deal with subsequently) I tried fusing the powdered minerals with cyanide of potassium. This was not at all satisfactory; at a low red heat a large amount of insoluble potassium tantalate and niobate was formed which enveloped the reduced tin so that it did not collect in globules. When the fusion was extracted with water there was left a porous mass which yielded up tin to hydrochloric acid, but a decided amount of the acids also went into solution. It is difficult to obtain crucibles or vessels of any size that will withstand the action of cyanide of potassium at a full red heat without being attacked. Knowing that alkaline tantalites and niobates *soluble in water* can only be obtained by using high temperatures in the fusion with caustic alkali, I next tried attacking the minerals with potassium carbonate at a high temperature in nickel and iron crucibles. This plan was successful to a certain extent, but the nickel and iron crucibles were seriously affected and scaled, externally by the action of the air, and internally by the manganese which was formed in the fusion. It then occurred to me that if the materials were heated at a high temperature in wrought-iron or steel vessels *in a reducing atmosphere*, not only would these difficulties disappear but that also one might expect to reduce all the tin, lead, antimony, &c., to the metallic state at the same time, and thus much trouble and uncertainty would be saved in the subsequent operations. When this plan was tried it more than answered my expectations, for while the tin, antimony, &c., appeared to be completely reduced, the iron and manganese were obtained as *protoxides in the form of a black heavy crystalline sand* which could be very easily separated from the soluble alkaline tantalate and niobate by treating with water. I also found that the *zirconia* which some of these minerals contain was separated apparently almost quantitatively when the washed crystalline protoxides were dissolved in dilute acids. In the first experiments small steel crucibles and covers "spun" in the lathe from sheet-metal were made use of, and these answer very well for quantities of mineral up to about 25 grms. These crucibles are 2½ inches high, 2½ inches broad at the top, and 1½ inches across the bottom. They are furnished with well-fitting covers which overhang the top of the crucible about three-

eighths of an inch. These crucibles are placed in a large fireclay or, preferably, in a plumbago crucible, and the space between them is packed round nearly to the top of the smaller crucible with wood charcoal in fine powder well rammed down. The remaining space is filled up with lumps of charcoal about the size of nuts, so that the exterior lid will just go on. The accompanying figure shows the arrangement.



A, The exterior crucible; B, the space filled with finely-powdered charcoal; C, the steel crucible and contents; D, the nut-like piece of charcoal.

The crucible is put into the furnace and slowly brought up to a red heat to partially frit the materials, and to allow much of the carbonic acid to escape while the mass is still porous. The heat is then raised, and maintained at the highest temperature the furnace will give for one hour. I use one of Griffin's excellent radial burner gas furnaces which yield a temperature equal to the fusion of cast-iron without any blast of air being required. The exterior vessel for the size of the small steel pots mentioned is a No. 4 Morgan's plumbago crucible. Recently I have procured some much larger steel pots and covers which are 7 inches high by 5½ inches diameter; these are pressed by hydraulic power out of steel one-eighth inch thick, and were made for me by Mr. McNeil, of the Kinning Park Ironworks, Glasgow. They require a No. 30 plumbago exterior crucible, and will deal with about a kilogram. of material at a time. When the crucible is opened after the fusion the contents generally come out in one fused compact piece without any trouble; the top portion has a yellow-white colour, while the bottom layer forms a black mass which can often be separated almost completely from the top one by a blow with a hammer. If the columbite or tantalite contains tin, as is almost invariably the case, the interior of the steel crucible is tinned over. Some of the tin is frequently found as a spongy metallic mass mixed with the black material, and often distinct globules and beads are noticed. The whole contents of the crucible slightly broken up in a mortar are now treated with about 500 cc. of water (for 25 grms. of the mineral) when the potassium tantalate and niobate pass rapidly into solution as they are very soluble, while the heavy black sand-like material mixed with a little tin, &c., settles down almost immediately, occupying very little space; above this there is a small amount of light green coloured precipitate which quickly turns brown in contact with the air. By leaving the whole quietly in a tall beaker for an hour about nine-tenths of the yellow liquid can be drawn off quite bright and clear, thus saving the trouble of filtering it. The remainder is stirred up with water, and leaving all the heavy material in the beaker the solution is filtered (best by the pump and the use of a toughened filter) till all the soluble matter is extracted. The small amount of precipitate on the filter is washed back on to the black sand in the beaker. The solution containing the potassium tantalate and niobate is always yellow or brown coloured, and contains traces of iron and manganese, probably as double potassium carbonates; this, however, does not afford any hindrance to the separation of the tantallic and niobic acids in a pure state. Under this rather severe treatment the

steel crucibles are not appreciably affected. I have made five or six successive fusions of 25 grms. of columbite in one of these small spun vessels without noticing any change except that the interior became rather heavily coated with tin. When this occurs it is well to discard them as they are so cheap rather than to run the risk of losing the contents. It does not appear to be necessary when working upon ordinary columbites and tantalites to add any reducing material to the contents of the crucible. With some of the stannic- or stibio-tantalites which contain much tin or antimony it may be advisable to add some black flux prepared from cream of tartar or similar material to the mixture. The minerals in this manner are resolved into two parts:—

A. A clear solution more or less yellow or brown coloured which contains nearly all the tantalalic and niobic acids mixed with traces of iron and manganese, but free from tin, antimony, lead, or other heavy metals.

B. A residue of black crystalline sandy matter containing nearly all the iron, manganese, and other bases mixed with some of the metals reducible by carbonic oxide or by the protoxides of iron and manganese, though most of these metals alloy and unite with the walls of the steel crucibles, especially when these are used for the first few times.

A. The solution is treated as follows:—When 25 grms. of mineral have been employed it will measure with the washings about 1 litre; to this is added a few cc. (four or five?) of potassium sulphide solution, and the whole well stirred up; this causes the liquid to become black. Rather more than enough pure hydrochloric acid than is equivalent to the potassium carbonate employed (80 to 100 cc.) is diluted with hot water to about a litre, and into this contained in a beaker holding 3 to 4 litres the black solution is poured with constant stirring. This causes a violent evolution of carbonic and sulphydric acids, and the tantalalic and niobic acids separate out as a white flocculent precipitate. The beaker is then placed in a water-bath and heated until the precipitated acids appear to settle, then allowed to cool, and the clear portion, which should be about five-sevenths of the whole, is drawn off with a syphon, and the acids repeatedly stirred up with hot water, and washed by decantation till the last washings show no sign of chlorine with silver solution. The niobic and tantalalic acids generally settle very quickly when thus treated, but occasionally they require a rather prolonged heating in the water-bath to make them do so. I have not been able to find out the cause of this; I have had two successive fusions treated exactly in the same way behave differently; one would settle quite easily even with cold water, while the other required considerable heating to make it do so. It does not save any time to try to filter these acids and so hasten the operation (at least with ordinary filters). The water passes through the filters readily enough, but it does not wash out the salts. Large cracks form, through which the wash-water runs unchanged. When the decanted wash-waters cease to contain any chloride the acids are brought upon a filter, dried at 100° C., and then pulverised. They then yield a pure white soft powder resembling oxide of zinc or magnesia. They contain no sulphuric acid, chlorine, or potassium, no iron, manganese, tin, or heavy metals, and as they dissolve almost immediately in cold hydrofluoric acid, oxalic acid, &c., they are in a condition eminently adapted for their separation by Marignac's process. The acids so obtained from the columbite from Middleton when dried at 100° C. gave, on strong ignition, 90·71 per cent of anhydrous acids and 9·29 per cent of water. When washing the precipitated tantalalic and niobic acids by decantation, the supernatant fluid is always opalescent, and in order to see what loss this may occasion, and also to ascertain how much iron and manganese were present in the yellow fluid from 20 grms. of columbite, I evaporated the whole amount of the washings to dryness in a platinum dish with a slight excess of sulphuric acid, on taking up with water and boiling, there was obtained 0·038 of ignited acids equal to 0·19 per cent on the columbite. In the

filtrate from this there was obtained 0·182 gm. of ferric oxide and 0·051 of manganese oxide, consequently the whole of the filtrates from 20 grms. of the Middleton columbite yielded from about 15 to 20 litres of washings:—

Tantalalic-niobic acids	0·038
Ferric oxide	0·182
Manganese oxide	0·051

Total 0·271 gm.

So that if the object is merely the preparation of tantalalic and niobic acids, it would obviously never pay to deal with these filtrates, but it shows how slight the solubility of the acids is in the small excess of hydrochloric acid employed, and also how small an amount of iron is really contained in the yellow or brown alkaline solutions. By this process I have not at present been able to trace with certainty the small amount of tungstic acid (0·26 per cent) which is said to exist in this Middleton columbite by Hermann, though in other analyses of this mineral it is not indicated. In order to ascertain what amount of carbonate of potassium is necessary I have made a good many trials with different proportions with columbites and tantalites; four parts of carbonate to one of mineral gave no better results than 3 to 1. Three parts of carbonate gave a slightly better yield than 2 to 1, and finally I found 2½ to 1 was as good as 3 to 1; so for ordinary columbites and tantalites these are the proportions I generally employ.

B. The black sandy matter which is left on treating the fusions with water is a mixture of ferrous oxide, manganous oxide, reduced iron, small globules of tin, zirconia, silica, &c. It oxidises rapidly on exposure to the air, and so it is advisable to wash it as speedily as possible from the alkaline tantalate and niobate, or ochreous precipitates form which pass the filters. It is treated with hydrochloric acid diluted with its own volume of water, when all the black sand-like matter dissolves at once, leaving some white residue undissolved. Generally there seems to be a little metallic iron present, since after the black matter has dissolved small particles are seen dissolving with strong evolution of hydrogen. The tin also is alloyed with iron, for it is very little attacked even by strong acid (Lassaigne, "Gmelin's Chem.," v., 314). As it is heavier than the white residue it is possible to separate it entirely from this by elutriation. The acid liquid, including the white matter, is then evaporated to dryness in a porcelain or glass basin and taken up with dilute hydrochloric acid, the insoluble matter is collected on a filter, washed, dried, and ignited. This material is yellowish white in colour. It varies in amount from different minerals and also somewhat with the temperature reached and the amount of potassium carbonate employed. In the case of the Middleton columbite it ranged from 5 to 7 per cent on the weight of the mineral started with, but about half of this was silica. 1·420 grms. of ignited residue treated with hydrofluoric and sulphuric acid, gave—

Matter insoluble in HF and H ₂ SO ₄	0·7195
Silica volatilised	0·7005

Total 1·4200

The material freed from silica was fused in a small platinum crucible at the highest temperature that could be obtained with a powerful blast lamp with an excess of potassium carbonate. Though the fusion was maintained for a long time and the carbonate volatilised rather freely, a considerable amount of the material would not dissolve but floated about in the fused carbonate. The fused mass was digested in water, when a heavy white precipitate remained undissolved; this was filtered off, washed, and treated with hydrochloric acid, which left it apparently unchanged. It was again filtered off, washed, dried, and ignited, when it weighed 0·310 gm. This was fused with sodium pyrosulphate, when it went entirely into solution and dissolved clear in water. This solution gave no sign at all of titanium with peroxide of hydrogen. It gave a

heavy gelatinous precipitate with ammonia which was readily soluble in excess of oxalic acid. The solution acidified with hydrochloric acid gave a very strong orange-red colour with turmeric paper, from which it may be inferred that the bulk at least of the material was *zirconia*. If this is all *zirconia* it would amount to 1.51 per cent on the columbite. The matter which was brought into solution on the fusion with potassium carbonate was found to be a mixture of tantalic acid, niobic acid, and a little titanic acid; it amounted to 0.4095 grm., equal to 2.047 per cent on the mineral employed. Consequently the insoluble matter in this case was composed of:—

Tantalic, niobic, titanic acids	0.4095
Zirconia (?)	0.3100
Silica	0.7005
Total	1.4200

The amount of pure white acids obtained was equal to 69.32 per cent of the anhydrides, and adding the 0.2 per cent in the wash-waters and the impure acid obtained from the insoluble matter, the total is 76.62 per cent on the mineral employed, which except for the silica agrees well with Chandler's analysis for Middleton columbite as given for comparison underneath:—

Niobic-tantalic acid	76.79
Stannic acid	0.60
Protoxide of iron	18.23
Protoxide of manganese	3.14
Oxide of copper	0.48
Undetermined	0.76
	100.00

The resistance which *zirconia* offers when fused with potassium carbonate is so remarkable that it seems to afford a means of separating it from other bodies. To test this insolubility directly, I fused 1 grm. of (so-called) chemically pure zirconium hydrate with 4 grms. of potassium carbonate for an hour at the highest temperature obtainable with a gas blast-lamp. On treating the fused material with water the aqueous solution was made slightly acid with hydrochloric acid, and ammonia then added in slight excess. No precipitate resulted. The insoluble *zirconia* was then gently boiled for four hours with hydrochloric acid and water in equal parts, keeping up the water from time to time. When this solution was filtered and a slight excess of ammonia added, there was a slight turbidity which in some hours deposited a few flocks of precipitate. These would certainly not weigh more than a milligram. or two. Considering how exceedingly difficult it is to prepare *really pure zirconia*, it is even doubtful whether this trace of precipitate was really *zirconia*. On looking up the literature of *zirconia*, I found that Venables and Clark (CHEMICAL NEWS, lxxiv., 43) in their study on the zirconates had previously arrived at the same conclusions. It is possible that this insolubility of *zirconia* may be utilised in the very difficult problem of its separation from titanic acid; it certainly seems to answer in this respect with tantalic and niobic acids.

To recapitulate, I have endeavoured to show—(1) That it is more profitable to dissolve away the tantalic and niobic acid in tantalites and columbites by the action of potassium carbonate at a high temperature than it is to reverse the process, and to dissolve away the bases from the acids with potassium or sodium pyrosulphates.

(2) That by working in this manner in a *reducing atmosphere*, platinum vessels can be replaced by steel crucibles with advantage, and also that such metals as tin, &c., are by this means effectually removed in the first operation instead of requiring continual tedious and uncertain re-fusions with alkaline sulphides.

(3) That any *zirconia* appears to remain entirely with the small portion of insoluble matter left after the fusion has been treated with acid, whereas when potassium pyrosulphate is employed, it is dissolved and is likely to be confounded with the acids as Chandler states. Of course it

is not put forward as a quantitative process, but it certainly yields acids which are much purer than those obtained by fusions with bisulphates. Since the tin and similar metals unite in great part with the vessels used, it is impossible to estimate them even approximately. When it is desired to do this, I proceed as follows:—Fuse the finely powdered mineral in a platinum crucible at a *high temperature* with three parts of pure potassium carbonate, extract all that will dissolve by digestion with a solution of citric acid at a gentle heat, filter and collect any insoluble matter on a filter, wash well, dry, and ignite it, then re-fuse it again with a smaller quantity of potassium carbonate, and treat again with citric acid solution. Everything now goes into solution except a little silica, *zirconia*, &c., which is filtered off, washed, and kept if necessary for further examination. Through the clear warm acid solution (which can be supersaturated with ammonia without causing any precipitation) hydric sulphide is passed to saturation, when the tin, antimony, &c., come down as sulphides. (By dissolving very small amounts of pure stannic and antimonious oxides in a large excess of citric acid, I could not trace that the presence of this acid impedes the precipitation). Filtering off the sulphides after washing, the solution, now free from heavy metals, can be used for the estimation of the tantalic and niobic acids as well as for the bases after the destruction of the citric acid.

With regard to the estimation of niobic acid in company with tantalic acid, I mentioned in a former paper (CHEMICAL NEWS, xcv., 1) some peculiarities observed when these acids are brought into solution with oxalic acid or oxalates. I have spent much time in endeavouring to utilise these reactions as a means for their separation, but I regret to say without any useful result. When they are associated the acids do not behave in the same manner as they do separately. At the time this prior paper was written, I was unaware that Russ (*Zeit. Anorg. Chem.*, xxxi., 42) had previously studied these oxalates, but he too comes to the conclusion that "The separation of tantalum and niobium by means of the complex oxalates cannot be effected." In my previous paper I also mentioned that I found that the hydrated tantalic and niobic acids can be brought into solution with *phosphoric acid*, and I showed that when such solutions were treated with zinc dust the niobic acid yielded intensely brown or black solutions. I have since noticed that these deeply coloured solutions are very much more permanent than those obtained with oxalic or other acids, and I have endeavoured to estimate the niobic acid by filtering the solutions in phosphoric acid through a column of zinc dust or spongy electrolytic zinc, receiving the deeply coloured niobous phosphate in a solution of ferric sulphate, in which the reduced iron is afterwards estimated by permanganate. Some difficulties in the manipulation of this process have been encountered, but an apparatus has been recently contrived by which the solutions can be digested with the zinc as long as may be desired, and finally filtered without any exposure to the air. When these experiments are concluded I hope in a further article to give an account of them. I believe that these steel crucibles, protected from oxidation in the way I have described, may find useful applications for opening up other minerals such as rutile, zircons, beryl, monazite, and zenotime.

Royal Institution.—On Tuesday next, January 19, at 3 o'clock, Prof. Karl Pearson begins a course of two lectures at the Royal Institution on "Albinism in Man"; on Thursday, January 21, Prof. J. O. Arnold commences a course of two lectures on "Mysteries of Metals"; and on Saturday, January 23, Prof. Sir Hubert Von Herkomer delivers the first of two lectures on (1) "The Critical Faculty," (2) "Sight and Seeing." The Friday Evening Discourse on January 22 will be delivered by Dr. Alfred Russel Wallace on "The World of Life as Visualised and Interpreted by Darwinism," and on January 29 by Colonel Sir Frederick L. Nathan on "Improvements in Production and Application of Gun-cotton and Nitro-glycerin."

THE NATURE OF CHEMICAL CHANGE.*

By HENRY E. ARMSTRONG.

"That which is far off and exceeding deep, who can find it out?"—*Ecclesiastes*, vii., 24.

"Le plus grand dérèglement de l'esprit est de croire les choses parce qu'on veut qu'elles soient."—*La Vie de Pasteur*: VALLERY-RADOT, p. 233.

NOTHING is more surprising than the apparent unwillingness of chemists to formulate a consistent and comprehensive theory of chemical change: the text-books are silent on the subject. Whatever service—and it is not inconsiderable—the ionic dissociation hypothesis may have rendered, it has not given us such a theory: its advocates tell us merely that, in the case of electrolytes, action takes place between the so-called ions, yet only on dry land as it were—on leaving the bath; what happens in the case of non-electrolytes we are not informed. Such a conclusion is at best little more than a statement that the action is between the acting units—a fairly evident proposition; of the process we learn nothing. Unfortunately phrases and phrases have taken the place of clear ideas in our text-books and every schoolboy prates of ions nowadays. I am tempted to apply Wordsworth's words to the situation:—

"No single volume permanent, no code,
No master spirit, no determined road
But equally a want of books and men."

In replying to the discussion which followed this communication, I took occasion to animadvert upon the lack of chemical feeling displayed by the adherents to the physical school and drew attention to the need of once more cultivating the use of fingers in the laboratory, remarking that we must have practical and not paper chemists if we were to regenerate our industries and to play the part the President of the Section had advocated in his Address. I mentioned that prominent representatives of industrial chemistry in Germany, in discussing the situation with me recently, had deplored the evil results which had followed from the unbalanced development of so-called physical chemistry, leading, as this has done, to the neglect of the practical side and the substitution of an off-hand attitude of superiority for that of careful unbiassed inquiry so characteristic in days gone by of the German school. The effect on the younger generation is disastrous, Paucity of judgment will only be recovered when this is admitted. It is essential that we should recognise that "physical chemistry" is at best only a very minor branch of our subject and that the special prominence which has been accorded to it of late years is, after all, largely the consequence of bold advertisement. Nowhere, in recent years, has the uncompromising worship of the cult of the ion—the elevation of the ion into the position of an icon—been more fashionable than in the United States of America: almost every text-book is devoted to the display of ionic rites, so that for years to come it will be useless to pray that youth be delivered from temptation.

Surely it were time that we cleared our minds of cant and set to work to introduce an element of philosophy into our science—that we swept aside the jargon which now disfigures our literature and substituted honest straightforward statements of fact or clear admissions of ignorance for the specious illusions which have too long been foisted upon the unwary student.

I venture to think that chemists need to be freed from the control of the pseudo-mathematical-physical speculations to which they have heedlessly subjected themselves of late years; that they need to give clear expression to that sense of feeling and knowledge of fact which is theirs and theirs alone in virtue of contact with actual materials in process of change. The speculations of the mathematician are very properly often guided by pure fancy—but chemists are bound to be realists. Our attitude too is

very different from that of the physicist,* who is concerned mainly with the mere gambols of molecules whose internal structure and interactions it is our province to study. Physicists appear to have no conception of the depths to which we have penetrated nor of the certainty of not a few of our methods, a certainty due to the fact that we are often able to pile up odds to such an extent that the formal correctness of our explanations becomes almost unquestionable. We need to cast off our subserviency to mathematical-physical speculation. The physicist is rightly prepared to give rein to his fancy and to propound hypotheses to the n^{th} degree of improbability merely in order that he may be able to give mathematical expression to his results. It is his way of recording as well as of advancing his position. We, however, are in no manner called upon either to be misled or to be carried away by the apparent agreement of hypothesis with fact when expressed in mathematical form. We have only to remember that there is an infinite power in mathematical expressions of cloaking ignorance as well as of summarising knowledge; that the same expression may be applicable to cases in which the operations are quite diverse in character or *vice versa*. Wendell Holmes must have had premonition of the reception that was to be accorded to the ionic dissociation hypothesis when he wrote the lines:—

"That boy with the grave mathematical look
Made believe that he had written a wonderful book
And the ROYAL SOCIETY thought it was true!
So they choose him right in; a good joke it was too!"

—*The Professor at the Breakfast Table*.

However much others may condemn our chemical feelings and our pedantic regard for facts in opposition to mathematical "let it be granted" fiction, let us not forget that it is our business to dissect and display the inner meaning of the phenomena of chemical change. We have been far too generous in allowing well-meaning speculators, who have in no way been conversant with the facts generally, to dictate a policy to us: it is to be hoped that we shall now once more take the control of our affairs into our own hands.

Since 1885, when I first brought the matter before the Chemical Section of the Association in my Address from the Chair, I have consistently maintained that the generalisation upon which we should base our conceptions of the nature of chemical change is that postulated by Faraday—namely, that chemical affinity and electricity are one and the same force. If this view be adopted, it follows that the conditions operative in electrolysis are equally operative in all chemical interchanges. The important step taken by Arrhenius in 1883 was the discovery of a practical method which appeared to correlate chemical with electrolytic activity.

It is noteworthy, however, that as far back as 1878, Ayrton and Perry contended that the electrical law of Ohm is the chemical law—or as they express it: "the quantity of chemical action in unit time equals the sum of a great number of terms, each of which is an electromotive force divided by a resistance." All that we know is in accordance with this view.

The dissociationist school, following Clausius, always contend that the apparent fact that any electromotive force, however small, will produce sensible electrolysis in the solution of an electrolyte is complete proof that free ions

* Chemistry and physics are necessarily interdependent disciplines—it is impossible to be a chemist without also being to some extent a physicist, although apparently the practice of physics is compatible with a complete disregard of chemistry. Chemistry did not become a science until it availed itself of the balance. Sooner or later, all properties must be quantified if an exact expression is to be given of their value; but the introduction of one or two new methods of measurement cannot be held to justify the treatment of measurement work as a separate discipline. Chemistry is a single science—the exclusive cultivation of any of the sections into which it may conveniently be divided must always conduce to narrowness of purview. The worker who is generally well informed and who applies his wide knowledge to the development of some special subject is the true specialist; such men are urgently required at the present day to restore the sense of proportion and to promote once more the development of the comparative and critical spirit among us.

* The introduction to a discussion on the subject in Section B (Chemistry) at the meeting in Dublin of the British Association for the Advancement of Science.

TABLE I.

Grm.-molecular proportion of solute.	Grms. of water per grm.-molecular proportion of solute.	Solute, HCl.		Solute, HNO ₃ .	
		Molecular conductivity.	Molecular hydrolytic activity.	Molecular conductivity.	Molecular hydrolytic activity.
0.05	20000	395.54	334.0	391.13	316.0
0.10	10000	391.57	340.0	383.07	326.0
1.00	1000	330.07	499.0	329.41	468.0
2.15	465.1	279.14	786.9	281.25	675.3
3.00	333.3	245.29	1122.0	250.29	864.3
5.00	200.0	183.05	—	191.26	—
6.00	166.7	158.22	—	169.48	—

are present in solution and that as these are transported by the current others are liberated spontaneously and take their place. I have always maintained that this interpretation should not be put on the facts. The experiment quoted by Helmholtz in his Faraday lecture, on which reliance is placed, is not a valid proof, as the means used to remove oxygen from the liquid (viz., a third electrode of palladium charged with hydrogen) could not effect this object completely: and some hydrogen would necessarily pass into solution, otherwise there would be no equilibrium; the inevitable consequence would be that the electrodes would remain more or less polarised. I even venture to think that the Helmholtz atomic charge hypothesis is entirely open to question. We have been taught to think of hypothetical simple ions—free ions—as carrying the charges; but in point of fact the bodies we charge are always highly complex viscous electrolytes of low conductivity; it may therefore be questioned whether there be any proof that individual ions can be charged, whether it be not more probable that the charge is always carried by a complex system.

The conditions in a solution are certainly by no means simple; in fact, it is little short of impossible to avoid the conclusion that behind the apparent simplicity of Faraday's law there is probably a give-and-take process at work of which no account can be rendered, the summation result of which alone has been taken into account in framing the hypothesis.

The atomic charge hypothesis, moreover, is not in accordance with our conceptions of valency. Thus in a series of oxides taken in the order of their heats of formation, commencing with those in the production of which but little heat is evolved, such as silver oxide, heat is developed if the metal in any one of the oxides be displaced by that of the oxide next below it in the series. If the two charges of the oxygen atom be given up in the formation of the initial term of the series, whence—it may be asked—is the energy derived which is liberated each time on passing to an oxide having a higher heat of formation? It cannot well be supposed that the oxygen remains a non-contributor and that the energy is derived from the metal alone; whatever the nature of the process, metal and oxygen are in some way reciprocal agents. In like manner, the properties of water are incompatible with the assumption that the two single charges of the two hydrogen atoms simply neutralise the two charges of the oxygen atom. Physicists have never attempted to deal with facts such as these.

The conception of a definite "valency volume" recently introduced by Barlow and Pope may well prove to be applicable to the problem: it is conceivable that the volume of material displaced in electrolysis is in some way proportional to the power of the displacing agent.

The majority if not all of the results arrived at by the application of the ionic dissociation hypothesis are independent of the fundamental premises which underlie it and depend merely on the recognition of the fact that the order in which electrolytes exercise their chemical activity is practically the order of their activity as electrical conductors in an electrolytic circuit. Any hypothesis which would satisfy this relationship might take its place; indeed, for many purposes of calculation, it is probably unnecessary to go further than to assume that it is established and

to make no hypothesis in explanation of the fact; whilst in cases in which it is necessary to go further, it is probable that the phenomena are by no means so simple as is supposed and that conclusions based on the application of the hypothesis cannot be accepted even provisionally.

The fact that discussion has been confined almost entirely to weak solutions has been a most fertile source of misconception: when all degrees of concentration are considered, results are arrived at which are by no means such as should follow from the premises adopted. Comparing, for example, electrical conductivity with hydrolytic activity—although the order of activity of a series of hydrolysts is that of their activity as electrolytes, in the one case (hydrolysis), there is a decrease, in the other (electrolysis) an increase of "molecular" activity as the concentration is diminished; furthermore, when nitric is compared with chlorhydric acid, whereas the hydrolytic activity of the nitric is always inferior to that of chlorhydric acid at all concentrations and the more so the weaker the solution—in the case of conductivity, in moderately and very dilute solutions chlorhydric acid is a better conductor than nitric acid but in concentrated solutions it is a worse conductor, the difference becoming the more pronounced the stronger the solution. The values given in Table I. have been obtained by Mr. Wheeler and myself in a set of preliminary experiments.

There is a well-known adage that you cannot have your cake and eat it: if conductivity and hydrolytic activity were both properties to be referred to the operations of dissociated ions, they should run not only on more or less parallel lines but also in similar directions: *in point of fact, they run in opposite directions*; it is rational, therefore, to assume that the two processes are essentially different in character, not similar as the dissociationist school would have us believe.

The Faraday theory of chemical change, as I propose to term it, involves the assumption that the conditions operative in a voltaic cell must be realised before any change can take place—that is to say, that a conducting system must be established consisting of at least three components; no less a number, I imagine, will afford a slope of potential. One of the components must be an electrolyte: of the two remaining members of the system, the one must be a substance—a metal, for example—with which the negative radicle of the electrolyte can be associated; the other may be either active or neutral (in the chemical sense) towards the positive radicle of the electrolyte. The only difference between the case of a voltaic battery and that of a chemical change taking place in a fluid mixture without electrodes is that in the battery conducting electrodes or feelers are introduced which enable us to tap the circuit and utilise the energy set free in the interactions. In a fluid medium, this energy is frittered down into heat: in any case, our chance of being able to utilise the energy of chemical change as electricity depends on our ability to interrupt the circuit by the interposition of conducting terminals.

The remarkable results arrived at by Dixon and by Brereton Baker with which, it may be supposed, all are familiar,* have always appeared to me to afford complete

* It is noteworthy that they are entirely disregarded by the ionic dissociationist school.

justification of the above conclusions. Baker's observations show that liquid water alone does not promote the interaction of hydrogen and oxygen gases; change only takes place when impurity is present—that is to say, when the water becomes a composite electrolyte. Larmor, in his recent Wilde Lecture, has dwelt on the probability of encounters taking place *between pairs* of the different molecules rather than between any greater number of molecules in a mixture of gases. I venture, however, to think that the experimental evidence is of so convincing a character that it may be affirmed that whatever the statistical probability of an effective meeting may be, the mating of the hydrogen and oxygen molecules is necessarily dependent on the advent of a suitable composite electrolyte: so that the patience of the molecules within the mixture must be exercised until proper opportunities occur for the interchange of affections—i.e., for affinity to operate; probably no great demand is made, because of the almost infinite rapidity with which molecular motion is propagated in gases, especially under compression.

From the point of view here advocated chemical interchanges are essentially all associative processes and their occurrence is dependent on the operation of a catalyst. But of late the doctrine has been promulgated that a catalyst is a substance which merely accelerates change—not one which directly conditions change; that the actions which take place more or less rapidly under the influence of catalysts also take place without them but so slowly that their occurrence cannot be detected in a measurable time. I venture to question this. Take the case of cane-sugar. Does anyone who has really worked with and learnt to appreciate this substance believe that any change would take place if the *pure* compound were dissolved in *pure* water and the solution were preserved in a *clean* vessel and *no acid impurity* were allowed to gain access to it? And yet a trace of acid would almost immediately condition a perceptible change in such a solution.

In solution, probably, the sugar is to some extent combined with water and certainly the water must be in intimate contact with its molecules: why then does not water act to an appreciable extent—why does acid produce such an effect? The dissociationists will answer:—Because there are so few hydrogen ions free in water,* and that the acid acts by increasing the proportion of hydrogen ions. But to what extent can a trace of acid be supposed to have this result? Its effect is altogether out of proportion to the extent to which, *ex hypothesi*, it can be supposed to furnish hydrogen ions.

But it may be and I contend has been *demonstrated* that hydrogen ions are *not* the effective cause of hydrolysis—in fact, the *selective action of enzymes is incompatible with the ionic explanation*. The effects produced by enzymes are in all respects comparable with those produced by acids, so that if the action of acids be exercised not by the acid molecules as wholes but by hydrogen ions liberated from them in solution, enzymes, in like manner, might be supposed to contribute hydrogen ions, in which case, since acids generally act on cane-sugar, enzymes generally should effect its hydrolysis; in point of fact, however, only one enzyme is known which has the power (invertase).

There is now abundant evidence to show that enzymes become associated with the particular substances which they hydrolyse and there is good reason to suppose that they act by carrying water into the circuit of change, delivering it exactly where it is required to effect the breakdown of the molecular complex. There is also good reason to suppose that acids act in a precisely similar manner—as true catalysts.

The effects produced by carriers, the use of which is so familiar to workers in organic chemistry, may be explained in a similar way.

(To be continued).

THE WIDE DISTRIBUTION OF SCANDIUM IN THE EARTH.

By Prof. G. EBERHARD.

UP to the present scandium has been numbered amongst the rarest of the elements occurring on the earth, so that but little is known of it, in spite of its obviously very interesting chemical properties. In fact, since the experiments of Nilson and Cleve, who obtained a few grms. of a scandium oxide which was not quite pure but still contained some ytterbium,* further work upon this element has not been published, undoubtedly only because of its great scarcity, while, moreover, the working up of the expensive minerals which are known to contain scandium, and which do not occur in great quantity—gadolinite, yttrite, euxenite—by uneconomical and uncertain methods (*e.g.*, fusing the nitrates), is a very tedious and troublesome process. Thus, according to the statements of Cleve (*Comptes Rendus*, 1879, lxxxix., 419) and Nilson (*Ber.*, 1880, xiii., 1439), the three above-named minerals contain only 0.001—0.0015, 0.0005, 0.02 per cent Sc_2O_3 respectively. Another difficulty is one which I encountered, namely, that euxenites from different sources do not always contain scandium, and, moreover, of gadolinites only that from Ytterby appears to contain it.

If it were concluded correctly from these facts that scandium is to be regarded as one of the rarest elements occurring on the earth, it would be all the more astonishing that outside the earth it undoubtedly occurs in other heavenly bodies in abundant quantities. Rowland, in the identification of the Fraunhofer lines of the sun's spectrum with those of known terrestrial elements, was able to detect with certainty some of the strongest scandium lines, and, moreover, the scandium lines appeared strongly in the spectrum of the sun. At the present time all the lines of this element, even the faintest, have been found with absolute certainty in the solar spectrum.

Moreover, not only in the solar absorption spectrum, but also in the emission spectrum of the sun's atmosphere (flash spectrum), seen for a few seconds during total solar eclipses, the strongest scandium lines have been recognised amongst those of the few elements occurring there. There can thus be no doubt that scandium is present in relative abundance in the sun.

The same is true of the stars. By examining their spectra it is found that the scandium lines appear plainly, and not only in those stars which resemble the sun. As soon as a star has advanced so far in its development that the number of lines in its spectrum is large (Vogel's Spectral Class I.a₃) the lines of scandium appear, generally very clearly. As an example, I may mention the star α -Persei, which has not yet reached the stage in which our sun now is. Also in the red stars, *e.g.*, α -Orionis and α -Herculis (Class III.a) which have long passed the state of the sun, the scandium lines are still visible and unaltered.

From the first it seemed clear to me that there cannot actually be this difference in the composition of the sun and stars on the one hand, and the earth on the other, as such a difference would contradict the cosmogonic theory, which assumes a common origin of all the heavenly bodies. It is rather to be supposed that scandium occurs more abundantly on the earth, if perhaps in a state of great dilution, and sufficient search has not been made for this element, or else it has been overlooked in analyses of minerals. It is only necessary to call to mind the analogous case of helium, which was long known to occur in the sun, but was not discovered on the earth till a much later date, owing to more refined methods of analysis.

When therefore in 1901, in measuring the spectrum of the stars, I observed the occurrence of the scandium lines, I decided that I would go deeper into the question, and search for scandium on the earth by a spectrographic

* The conclusion, based on Kohlrausch's observations, that there are free ions in pure water is quite illogical: the experiments do not justify it and it is impossible to admit that *pure* water has ever been examined or ever will be.

* Exner and Haschek in their investigation of arc spectra (p. 145) have found ytterbium in Nilson's scandium, and I myself have found a not inappreciable amount of ytterbium and thorium in Cleve's scandium.

method. As it was evident that this element would occur in a state of great dilution in the crust of the earth, I first tried to obtain information about the sensitiveness of the spectral reaction of scandium, so as not to work in vain. As I had no scandium at that time, after thorough practical study of the chemistry of the rare earths, I chose, to settle the question, one of those minerals which are known to contain scandium. When 0.1 grm. of the oxides of two different yttriotitanites (Nos. 247 and 248) were vaporised in the arc, both showed very plainly the principal scandium lines. They were also still plainly visible after I had diluted the oxides to one-tenth the strength with yttrium earths free from scandium, and again vaporised 0.1 grm. of this preparation. As according to Cleve the oxides of yttriotitanite contain 0.005 per cent Sc_2O_3 , the spectral reaction of scandium must be regarded as extraordinarily sensitive, even if the yttriotitanite oxides contain ten times as much scandium as Cleve states, which, according to my experience, seems to be the case. In any case, on the ground of this experiment, it seemed very promising to proceed to the spectrographic examination of minerals for scandium.

I first used minerals in which, according to the experiments of Nilson and Cleve, scandium might be supposed to occur, euxenite (Nos. 214 and 217) and gadolinite (Nos. 226 and 227) without, however, detecting this element. This was the case when I examined a piece of gadolinite from Ytterby, most kindly sent to me by Dr. Benedicks (Upsala), but here I observed phenomena which surprised me, and which led me to perform further experiments. After three extractions of the very finely divided mineral, the unextracted part contained considerable amounts of alumina and beryllium earth. (All the gadolinites examined by me contained beryllium earth, in spite of the statements to the contrary in literature). Moreover, the scandium lines appeared in the arc not much fainter than in the part which had gone into solution, while the lines of the rare earths, and especially those of yttrium, had been much weakened. This behaviour of the unextracted part led me to suppose that the feldspar-like matrix adhering to the gadolinite, which I had not removed in the working up of the mineral, and which cannot be extracted with acids, must be a silicate of alumina containing beryllium and scandium, for pure gadolinite would be completely extracted by the three processes.

To test this supposition, I asked Dr. Benedicks for specimens of the matrix rocks of Ytterby gadolinite, and meanwhile investigated another beryllium alumina silicate, a smaragd (No. 25) which I happened to have. It contained easily detectable quantities of scandium, and, moreover, the other rocks found in the Ytterby mine, feldspar, mica, and mica-schist, contained scandium, the last two to a considerable extent. Thus, for the first time it was proved that scandium might occur in other minerals as well as in those of the rare earths, and simultaneously the direction in which further search for scandium should be made was indicated. It was found that this element was present in a series of beryllium minerals and of micas. Among the micas tested, zinnwaldite from Zinnwald in the Ore Mountains contained specially large amounts of scandium, and when I examined whether other minerals from Zinnwald also contained scandium I found a great number contained this element, among them tinstone (SnO_2) and wolframite, which occur in large quantities and are rich in scandium.

But if micas contain scandium, rocks of which mica (especially biotite) forms an essential constituent, e.g., granite, gneiss, mica-schist, &c., must also contain scandium. This conclusion I also confirmed, thanks to the extraordinary spectral sensitiveness of scandium in the great majority of cases, and I now undertook the examination of as many different kinds of minerals and rocks as I could obtain from all possible places upon the earth, to see if they contained scandium, in order to acquire an adequate knowledge of the occurrence of this element, which had hitherto been thought to be so rare.

Before I give the results obtained I will make some remarks upon the details of the experiments. The minerals of the rare earths, especially the titanates, niobates, &c., give a spectrum which is so extraordinarily rich in lines that they must be worked up chemically before their spectra are photographed; i.e., must be decomposed into their chief constituents. (Prof. R. J. Meyer, Berlin, very kindly performed for me in his laboratory part of the very tedious and lengthy extraction processes. This renowned authority upon the chemistry of the rare earths often gave me valuable advice upon the further working up of the rare earths, and I am glad to take this opportunity of expressing my thanks to him). The part which could be extracted with acids was first separated from the non-extractable part, and the former was then further separated by treatment with oxalic acid into a part which was precipitated by this acid, and a part which was not precipitated by oxalic acid but gave a precipitate with ammonia. This precipitation of the remaining liquors with ammonia was always necessary, as scandium oxalate is exceedingly soluble even in weak mineral acids, such as the extraction always contains, and thus a part of the scandium remains in the liquid after precipitation with oxalic acid. The rare earths precipitated with oxalic acid were subjected to many other processes (precipitations, fractional crystallisations) to concentrate the scandium, but I will not now go into the details of these operations.

The preparation of other minerals and rocks was essentially simpler. They were first finely powdered and then heated to a bright red heat for some time in a porcelain crucible to remove the gases and water contained in them. If this preliminary treatment is neglected unpowdered particles spirt with little explosions, and powdered pieces crumble up as soon as the arc is started.

All preparations were vaporised with the same strength of current so as to obtain spectra under the same conditions, and a comparatively strong current was chosen 20 A. at 120 volts), because some minerals, e.g., quartz, zircon, bauxite, &c., are thoroughly vaporised only at high current strengths. The vaporisation is carried out in ordinary somewhat hollowed out arc lamp carbons, as with currents between 5 and 40 ampères I could not, with the rods of far purer Acheson graphite given me by Prof. Muthmann (Munich), get anything but a very strongly hissing, unsteady, and easily interrupted arc. Two precautions are so important for taking the photographs that failure usually follows their neglect. First, large quantities of material (in my experiments about 0.5 grm.) must be vaporised, as scandium mostly occurs only in extremely small amounts in the minerals, and only when large amounts of material are used are its spectral lines visible (in the photographs). But when such large quantities of substance are vaporised on the arc carbon, generally a fairly bright continuous spectrum appears, which would completely mask the faint scandium lines. Therefore a spectrograph with very large dispersion must be used to efface the continuous spectrum sufficiently. I took the spectra with a concave grating apparatus of the observatory (*Zeitschrift für Instrumentenkunde*, 1905, xxv., p. 371) and by means of it could practically completely suppress the continuous spectrum.

The second condition necessary for the success of the experiment is that the substance put in the arc carbon must be completely vaporised until all spectral lines disappear, which can easily be seen by observing the arc with a good pocket spectroscope. The vaporisation of rocks in the arc corresponds to a fractional distillation, the greater part of the most volatile constituents (e.g., the alkalis) vaporises at the beginning of the process, while most of the difficultly vaporised constituents, to which scandium belongs, vaporise quite at the end. If then a large quantity of mineral were put on to the arc carbon, and the photographs of the spectrum were taken as soon as a small portion or the substance had vaporised, no indication of the less volatile elements (e.g., Sc, Zr, Th, Ta) would be obtained in the resulting spectrum if they

were not present in very large quantities in the mineral, and thus an incorrect view of the composition of the mineral would be obtained. This mistake has very often been made, and to it alone is due our ignorance concerning the occurrence of scandium on the earth.

After these preliminary remarks I give here the minerals and rocks investigated by me. (Here the author gives a table of 366 minerals and rocks).

In 131 of them scandium was absent.				
" 50	"	"	"	doubtful.
" 103	"	"	"	visible.
" 62	"	"	"	easily visible.
" 20	"	"	"	strong.

366

In 220 of these minerals the presence of rare earths was undetected, in 36 of these minerals the presence of rare earths was doubtful, and in 110 rare earths were detected.

The chief result of the data given in the table is the surprising fact of the *universal occurrence of scandium on the earth*. In almost all rocks from which the mountains of the earth, or rather the chief parts of the earth's crust are formed scandium can be detected, and it is no longer a rare element, but, on the contrary, is widely and abundantly distributed, like only a very small number of other known elements. I am of the opinion that it would also be found in the rocks in which I did not find it, if larger quantities of material than I used were vaporised in the arc.

From this proof of the universal distribution of scandium on the earth it is no longer strange, but natural, that it should be found everywhere in the stars and the sun.

It may be of interest to mention that the meteoric stone of Pultusk, which to a certain extent forms a transition from the earth to the stars, contains a smaller amount of scandium than most of the earth's rocks which I investigated.

Other conclusions may be drawn besides this important result. It is evident from the table, as was to be foreseen, that among the known minerals a true scandium ore, i.e., a mineral which contains scandium as an essential and not merely an accessory constituent, has not yet been found by me. On the other hand, it appears that scandium may occur in many different minerals, if it is not a *necessary* constituent. Those in which scandium is to be found most frequently are the zircon minerals, beryls, the titanates, niobates, and titanoniobates of the rare earths, tin stone, tungsten ores, and micas. The quantity of scandium in these minerals varies within wide limits, but with a few exceptions it is always so very small that chemical analysis can hardly detect it.

The minerals which occur freely and which contain the most scandium are some euxenites and ytrotitanites, micas from the Ytterby mine, tin stone and wolframite from Zinnwald in the Ore Mountains. The last named mineral, according to a quantitative analysis by Prof. R. J. Meyer, confirmed spectrographically by me, contains about 0.2 per cent Sc_2O_3 ; thus an amount which is at least ten times greater than that of euxenite and ytrotitanite, so that there is no longer any obstacle to the preparation of larger quantities of the element. There seems to be no rule about the occurrence of scandium in the minerals. When a large piece of gangue from Hitterö, which consisted of feldspar, quartz, biotite, iron ore, orthite, gadolinite, malacon, thorite, was examined, I found scandium in the biotite and malacon, but not in the orthite, gadolinite, and thorite, which contain the rare earths, where it would be expected according to our former knowledge of the properties of this element.

There seems, moreover, to be no rule about the occurrence of scandium in rocks. It is to be found in rocks of all possible chemical composition and petrographic constitution. The amount of scandium is also subject to considerable variations, but is always exceedingly small. In some cases the amount of scandium seems to be pro-

portional to the amount of mica which belongs to the essential constituents of the rock. This is the case, for example, with many granites. On the other hand, however, some mica schists have not as much scandium in them as would be expected according to this, and if garnets have separated the mica schist has become free from scandium and all the latter has gone into the garnets.

The wide geographical distribution of minerals and rocks containing scandium indicates that there is no rule for the occurrence of scandium from a geological point of view. As a matter of fact it is immaterial for the occurrence of this element whether the rocks are of sedimentary, plutonic, or volcanic origin, and whether they were formed before the beginning of historical geology (archaic rocks) or at the present time (Vesuvius lava). The table contains rocks which were formed in the most different geological periods, although there is no apparent difference as regards the scandium. Also geological processes, such as endogenous and exogenous, contact metamorphism, impregnation metamorphism, pneumatolysis, are without apparent influence upon the occurrence of this interesting element. The same holds good of the neighbourhood of radio-active minerals, as the investigation of the minerals and rocks of Joachimsthal and Johanngeorgenstadt shows. All these negative results in the study of the laws regulating the occurrence of scandium, both from a mineralogical and geological point of view, indicate that scandium must be a very widely distributed element on the earth, like iron, which is found everywhere. It may be remarked here that the distribution of the rare earths seems to be exceedingly general. I have made observations on the occurrence of these elements in this research, and as lanthanum and yttrium have a very great spectral sensitiveness I have very often detected the rare earths, mostly with scandium. However, this last element may occur *without* the rare earths, and this is perhaps a support of Urbain's view, that scandium is not to be reckoned amongst the rare earths. For the chief characteristic of these elements is that they are always present simultaneously in numbers, if in relatively different quantities. No case is known in which one of the elements of this group occurs alone without being accompanied by at least one of the others, which is actually the case with scandium.

After it has been found possible owing to the foregoing work to obtain larger quantities of scandium it is to be hoped that this element will be subjected to a thorough chemical and especially physicochemical investigation. (NOTE.—This investigation has meanwhile been begun by Prof. R. J. Meyer, with great success). I have repeatedly convinced myself in the course of the chemical preliminary operations for the above investigation that the chemical properties of scandium are only very imperfectly known, and that scandium must have many reactions which are not yet generally known.

I have further examined the occurrence of large quantities of scandium in and near Zinnwald in the Ore Mountains, a research which has given results of great interest geologically and of general importance, but this investigation cannot be finished until I have collected a large series of rocks and minerals (which up to the present I have not been able to obtain). Hence the publication of the results so far obtained will be deferred till the research is finished.

I have been enabled to carry through this investigation by the kindness of my late chief, Geheimrat Vogel, who procured me the means of obtaining research material, of Dr. Credner (Leipzig), and Dr. Benedicks (Upsala), who sent me some rocks and minerals which were of great value for my work. I offer them all my hearty thanks. —*Sitzungsber. der K. Preuss. Akad. der Wissenschaften*, xxxviii., 851, July 23, 1908.

(NOTE.—While this article was in the press I heard of a Note (*Proc. Royal Soc.*, London, lxxx., p. 516) by Sir William Crookes, who has recently prepared scandium from the very rare mineral wiikite).

THE CORROSION OF IRON.*

By ALLERTON S. CUSHMAN,
Assistant Director, Office of Public Roads, Dept. of Agriculture, U.S.A.

(Continued from p. 17).

The Action of Hydrogen Peroxide on Iron.

PERHAPS the most conclusive proof that electrolytic action must take place before rusting can occur is given by an experiment of Moody's, which has been repeated and confirmed by the writer. Dunstan and his co-workers claimed that when iron is placed in hydrogen peroxide the metal is rapidly oxidised, with formation of ferric hydroxide. As Moody has pointed out, commercial hydrogen peroxide is invariably acid and contains impurities. In perfectly pure hydrogen peroxide bright iron will catalytically disengage oxygen and retain its polished surface unacted upon. It is not an easy matter to prepare a perfectly neutral pure solution of hydrogen peroxide, but it can be accomplished by two fractional distillations at 85° C. under reduced pressure (700 mm.) of commercial dioxigen. Before distilling the second time the solution should be made barely alkaline with a few drops of one-hundredth normal potassium hydroxide. In a pure neutral 1 per cent solution of hydrogen peroxide thus prepared, Moody's observation was confirmed. Iron immersed in the solution remained bright for a protracted period. Hydrogen ions do not exist in a pure neutral solution of peroxide; therefore neither solution of iron nor electrolysis can take place. If the flask containing the specimens covered by pure hydrogen peroxide solution is connected to a vacuum pump, oxygen is disengaged freely and boils off the surface of the metal without the appearance of the slightest speck of rust.

Reduced to its simplest terms, the following explanation of the rusting and corrosion of iron seems to the writer the only one that is tenable. In order that rust should be formed iron must go into solution and hydrogen must be given off in the presence of oxygen or certain oxidising agents. This presumes electrolytic action, as every iron ion that appears at a certain spot demands the disappearance of a hydrogen ion at another, with a consequent formation of gaseous hydrogen. The gaseous hydrogen is rarely visible in the process of rusting, owing to the rather high solubility and great diffusive power of this element. Substances which increase the concentration of hydrogen ions, such as acids and acid salts, stimulate corrosion, while substances which increase the concentration of hydroxyl ions inhibit it. Chromic acid and its salts inhibit corrosion by producing a polarising or dampening effect which prevents the solution of iron and the separation of hydrogen.

Demonstration of Electrolytic Action.

Early in this investigation the writer observed that whenever a specimen of iron or steel is immersed in water or a dilute neutral solution of an electrolyte to which a few drops of phenolphthalein indicator had been added, a pink colour is developed. If the solution is allowed to stand perfectly quiet it will be noticed that the pink colour is confined to certain spots or nodes on the surface. The pink colour of the indicator is a proof of the presence of hydroxyl ions and thus indicates the negative poles. Many persons who are interested in the metallurgical problems connected with the iron and steel industry may not be familiar with the modern theory of indicators, and therefore an explanation of the manner in which phenolphthalein shows the presence of hydroxyl ions by the formation of a pink colour will not be out of place. Phthalic acid was first prepared by Laurent in 1836 by the oxidation of naphthalene, and was first called naphthalinic acid. It was afterwards shown that the compound was not directly related to the naphthalene structure, and Laurent changed the name to phthalic acid, the derivatives of which became

known later as phthaleins. Phenolphthalein is a product which is formed by the condensation of two molecules of phenol or carbolic acid with the anhydride of phthalic acid. It is in its nature so weak an acid that it is not dissociated in solution, and as the molecule is colourless, no colour is seen when it is added to a perfectly neutral solution. If, however, an alkali is added the corresponding salt of the weak acid is formed, which immediately dissociates with the formation of a colourless metallic cation and the strongly rose-coloured organic anion. Thus all hydroxides of basic elements will show the pink colour in solution, even when present in only the slightest excess. On this account phenolphthalein is an exceedingly delicate indicator of the presence of hydroxyl ions.

Since phenolphthalein shows only the nodes where solution of iron and subsequent oxidation can not take place, Prof. W. H. Walker suggested the addition of a trace of potassium ferricyanide to the reacting solution, in order to furnish an indicator for the ferrous ions whose appearance mark the positive poles (see Note). If iron goes into solution, ferrous ions must appear, which, with ferricyanide, form the well-known Turnbull's blue compound. Going a step further, Walker suggested stiffening the reagent with gelatin and agar-agar, so as to prevent diffusion and preserve the effects produced. For this combined reagent, which indicates at one and the same time the appearance of hydroxyl and ferrous ions at opposite poles, the writer has suggested for the sake of brevity the name "ferroxyl." The reagent is prepared and used in the following manner:—A hot solution of the purest agar-agar or gelatin in distilled water is carefully neutralised with one-hundredth normal potassium hydroxide, using phenolphthalein as the indicator. When exact neutrality has been obtained a few drops of a dilute solution of potassium ferricyanide is added. When a layer of the reagent is poured into a dry Petri dish floating in ice water it should stiffen into a firm jelly in a few minutes. The polished specimens are laid carefully on the jelly and flooded with another layer of the reagent. After the preparation has hardened it should be covered and set away in a cool, dark place. In the course of a few hours the negative and positive zones will begin to develop in red and blue. If the reagent has been properly prepared the colour effects are strong and beautiful. In the course of a few days the maximum degree of beauty in the colours is obtained, after which gradual deterioration sets in.

(NOTE.—Phenolphthalein is used to a large extent in empirical tests, as in dairying, the cement industry, soil examinations, &c. The name is cumbersome if not alarming to the layman, while the chemist does not need to be reminded of the origin of the compound each time he has occasion to speak of it. A shortening of the name of the indicator to "phenolin" would be a decided improvement).

In the pink zones, as would naturally be expected, the iron remains quite bright as long as the pink colour persists. In the blue zones the iron passes into solution and continually oxidises, with a resulting formation of rust. Even the purest iron develops the nodes in the ferroxyl indicator, but impure and badly segregated metal develops the colours with greater rapidity and with bolder outlines. This result would of course be expected, as in pure iron the formation of poles would be conditioned by a much more delicate equilibrium than in impure iron, where changes in concentration of the dissolved impurities would stimulate the electrolytic effects. Even so-called chemically pure iron contains small quantities of dissolved gases, and it is not improbable that even slight variations in the physical homogeneity of pure iron will occasion the electrolytic effects which are made visible by this delicate reagent.

It has been noted by a number of investigators that different samples of iron and steel do not rust in the same way when subjected to the action of water and air. While some samples show localised electrolytic action, as indicated by deep pitting, others become covered with a more or less homogeneous coating of hydroxide, which

* Bulletin No. 30, U.S. Department of Agriculture, Office of Public Roads.

shows little or no tendency to localise in spots or nodes. The question naturally arises: In what respect do these two methods of rust formation differ? In the ferroxyl tests, when the colours first developed, two dark blue nodes formed at the opposite ends of the test-piece, with a large pink area in the centre, where for a time the metal remained quite bright. Very shortly, however, the poles changed, and the pink central area disappeared and gave way to a large blue node which enveloped three-quarters of the test-piece, with a small opposed pinkish spot. Again and again a reversal and change of poles took place. There were at least five such changes. As a result of this action the metal strip was rapidly covered over its entire surface with the same superficial, loosely adherent coating of hydroxide, which is obtained in many cases when certain samples of iron and steel are allowed to rust under a layer of water. It is presumable that as the surface of the metal is eaten into by the solution of the iron at the positive poles, a new condition of equilibrium occurs, resulting in changes and even reversals of the positive and negative nodes. This would indicate that in the case of metals which suffer from local action or pitting the segregation conditions are of a different nature from those which exist in the case of metals which rust more evenly. A rough analogy may be drawn by imagining an imperfect mixture of black and white sand, the respective grains of which may lie in streaks, spots, and layers, or may tend to arrange themselves in some more or less uniform relation to each other. The best demonstration that the rusting and corrosion of iron and steel in all its forms is essentially an electrolytic phenomenon is afforded by the fact that it has not as yet been possible to find a specimen of such purity that no trace of positive and negative nodes will be formed in the ferroxyl indicator.

(To be continued).

CORRESPONDENCE.

POTENTIAL ENERGY OF THE ELEMENTS.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS of September 4, 1908 (vol. xcvi., p. 120) I find a letter by Mr. D. J. Rankin on the "Potential Energy of the Elements." The following table is given:—

	K.	Atomic weight.
Helium	134.487	4
Sodium	23.338	22.88
Calcium	13.415	39.71
Strontium	6.141	86.94
Barium	2.516	136.4

A simple relationship exists between the numbers in each column. The ratio of the chemical potentials is 6 to 1 approximately for helium-sodium, and taking the column downwards 2 to 1 approximately. In the second column, that of the atomic weights, the ratios are approximately the same reversed.—I am, &c.,

J. C. THOMLINSON.

6, Villa View, Low Fell, Gateshead,
December 25th, 1908.

Method of Preparing Ethylene Hydrocarbons from Ether Salts.—Albert Colson.—When ethyl benzoate is heated in a sealed tube to 300° it remains unaltered, but at a temperature of from 305–310° it decomposes into benzoic acid and ethylene, $C_6H_5.CO_2.C_2H_5 = C_6H_5.CO_2.H + C_2H_4$. The vapour tension of the ethylene formed appears to remain constant at 310°. Stearic ether also undergoes the same decomposition, while the ethers of mineral acids similarly give the ethylene hydrocarbon. Thus the usual method of preparing ethylene is not an isolated example, but is a particular case of this general reaction.—*Comptes Rendus*, cxlvii., No. 22.

NOTICES OF BOOKS.

Laboratory Manual of Qualitative Analysis. By WILHELM SEGERBLUM, A.B. New York, London, Bombay, and Calcutta: Longmans, Green, and Co. 1908.

THIS manual on qualitative analysis will be found to inculcate useful virtues in the student, and can be recommended as giving a very suitable scheme of study in analytical work. The bases and acids are divided into the usual groups, and all the commoner inorganic acid radicals are treated, and in addition the three organic acids—oxalic, acetic, and tartaric. Both simple salts and mixtures are included, and in the case of practically every reaction the equation is given; it would, however, be better if all the equations for each group were not collected in separate sections, for the student is thus tempted to skip them altogether. The schemes for the separation of different members of the same group are particularly clear, and notes are given on special difficulties or the reasons for possible failures; the importance of preliminary work on each group is emphasised, and every endeavour is made to impress upon the student the need for thought and care in qualitative analysis. A collection of questions, mostly perhaps rather too simple and obvious, is included on the reasons for the various steps, and the student is given no excuse for mechanical or slovenly work. A course of collateral reading from the standard works on analysis is suggested in an appendix.

Practical Sanitation. By GEORGE REID, M.D., D.P.H. With an Appendix on Sanitary Law by HERBERT MANLEY, M.A. (Cantab.), M.B., D.P.H. Fourteenth Edition. London: Charles Griffin and Company, Ltd. 1908.

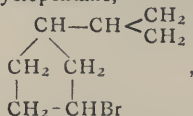
ALTHOUGH described as a new edition this is only a reprint of the last which was issued, and noticed in these columns not much more than eighteen months ago. The appendix on sanitary law which was entirely re-written for the last edition is reproduced, and gives very clearly the chief provisions of the law relating to the duties of sanitary inspectors, with explanatory comments.

A Text-book of Inorganic Chemistry. By Dr. A. F. HOLLEMAN. Issued in English in co-operation with HERMON CHARLES COOPER. Third English Edition. New York: John Wiley and Son. London: Chapman and Hall, Ltd. 1908.

THE third English edition of this text-book has been thoroughly revised, many chapters on subjects which have recently undergone rapid development being almost entirely re-written. It has been brought up to the latest possible date, as shown by the numerous references to work which has been published within the last few months—for instance, the solidification of helium is mentioned. A section on the metal ammonia compounds, which Prof. Werner has revised, gives an excellent summary of this complicated subject. The text is always interesting, and the author's lucidity and graphic style cannot fail to make the impression produced on the mind both deep and lasting. Perhaps as a necessary corollary it must be added that occasionally the author shows a disposition to dogmatise and state as positive facts some observations which are still under investigation; for example, from reading the chapter on the radio-active elements the opinion would certainly be formed that the degradation of copper to lithium is a perfectly well established and universally accepted fact. The great extent of the subject which is covered suggests that sometimes the treatment is sketchy, although perhaps this epithet can hardly be correctly applied to the great majority of the short sections in which the author's genius for picking out the salient points and throwing aside unnecessary details is well exhibited. The book is an interesting and essentially modern text-book of inorganic chemistry which first year students may use with advantage.

$$\begin{array}{c} \text{CH}-\text{CH} < \begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \end{array} \\ / \quad \backslash \\ \text{CH}_2 \quad \text{CH}_2 \\ | \quad | \\ \text{CH}_2-\text{CH}-\text{CO}-\text{NH}_2 \end{array}$$

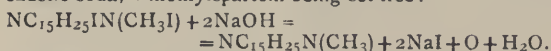
This view they have now proved to be correct by synthetical methods. β -Isopropylcyclopentanone, which is the ultimate product of the degradation of the amide molecule, when hydrogenated gives a secondary alcohol which is identical with that obtained by treating the amide derivative of camphenylone with nitrous acid. When heated to 100° with hydrobromic acid saturated at 0°, the alcohol yields β -isopropylbromocyclopentane,—



and this when subjected to Grignard's reaction gives β -isopropylcyclopentane carboxylic acid, from which by the action of phosphorus pentachloride and ammonia an amide identical with that derived from camphenylone can be prepared. The authors have not yet succeeded in passing from this compound to camphenylone itself.

Action of Sulphuric Acid on Aldehyde and Paraldehyde. Preparation of Crotonic Aldehyde.—Marcel Delépine.—When aldehyde vapour is led by a current of gas into an excess of concentrated sulphuric acid at 10–15° it is absorbed without any signs of charring, and on diluting the liquid with ten parts of water and distilling, large quantities of crotonic aldehyde are formed. Also when paraldehyde is dissolved in concentrated sulphuric acid, the liquid is diluted and distilled, crotonic aldehyde passes over in the first portions, and at the same time the polymer $\text{C}_8\text{H}_{12}\text{O}_2$ is obtained.

Action of Acids on Diiodo- α -methylspartein.—Amand Valeur.—Diiodo- α -methylspartein, which is really the iodomethylate of an iodoisopartein, $\text{NC}_{15}\text{H}_{25}\text{IN} \begin{array}{l} \nearrow \text{CH}_3 \\ \searrow \text{I} \end{array}$, when dissolved in dilute sulphuric, hydrochloric, or acetic acid, does not give the corresponding sulphate, &c., but a compound containing three atoms of iodine of formula $\text{HI} \cdot \text{NC}_{15}\text{H}_{25}\text{IN} \begin{array}{l} \nearrow \text{CH}_3 \\ \searrow \text{I} \end{array}$. Probably hydriodic acid is first set free, and it then reacts with the unaltered iodomethylate to give this compound. HI can also be removed by boiling caustic soda, α -methylspartein being set free:—



MISCELLANEOUS.

Iron and Steel Institute.—The Andrew Carnegie Research Scholarship.—A Research Scholarship or Scholarships, of such value as may appear expedient to the Council of the Iron and Steel Institute from time to time founded by Mr. Andrew Carnegie (Past-President), who has presented to the Iron and Steel Institute eighty-nine one-thousand dollar (5 per cent) Debenture Bonds for the purpose, will be awarded annually, irrespective of sex or nationality, on the recommendation of the Council of the Institute. Candidates, who must be under thirty-five years of age, must apply on a special form before the end of February to the Secretary of the Institute. The object of this scheme of Scholarships is not to facilitate ordinary collegiate studies, but to enable students, who have passed through a college curriculum or have been trained in industrial establishments, to conduct researches in the metallurgy of iron and steel and allied subjects, with the view of aiding its advance or its application to industry. There is no restriction as to the place of research which may be selected, whether university, technical school, or works, provided it be properly equipped for the prosecution of metallurgical investigations. The appointment to a Scholarship shall be for one year, but the Council may at their discretion renew the Scholarship for a further period instead of proceeding to a new election. The results of the research shall be communicated to the Iron and Steel

Institute in the form of a Paper to be submitted to the Annual General Meeting of members, and if the Council consider the Paper to be of sufficient merit, the Andrew Carnegie Gold Medal shall be awarded to its author. Should the Paper in any year not be of sufficient merit, the Medal will not be awarded in that year.

Memorial to Sir George Livesey.—With reference to the steps it has been decided to take to perpetuate the memory of the late Sir George Livesey, the Committee having the matter in hand desire to announce that contributions to the Fund should be sent to the Secretary of the Institution of Gas Engineers, 39, Victoria Street, Westminster. A sum of at least £10,000 is required for the object in view—the endowment of a Livesey Professorship in Gas Engineering and Fuel at the Leeds University—and contributions both small and large will be welcomed. Having regard to the great services which Sir George Livesey rendered the industrial world, and indeed to all classes of the community, it is felt that there will be a general desire throughout the country to do honour to his memory.

NOTES AND QUERIES.

Lantern Slides.—Can any reader inform me whether there is a firm having for hire lantern slides illustrating any chemical industries, as, for example, the manufacture of sulphuric acid.—T.O.B.B.

MEETINGS FOR THE WEEK.

MONDAY, 18th.—Royal Society of Arts, 8. (Cantor Lecture). "Public Supply of Electric Power in the United Kingdom," by G. L. Addenbrooke.

TUESDAY, 19th.—Royal Institution, 3. "Albinism in Man," by Prof. Karl Pearson, F.R.S.

WEDNESDAY 20th.—Royal Society of Arts, 8. "Gothic Art in Spain," by H. C. Brewer.

— Microscopical, 8. Presidential Address, "On Seeds, with Special Reference to British Plants," by the Rt. Hon. Lord Avebury. Exhibition of Foraminifera dredged from off the coast of Somaliland.

THURSDAY, 21st.—Royal Institution, 3. "Mysteries of Metals," by Prof. J. O. Arnold.

— Chemical, 8.30. "Organic Derivatives of Silicon—Part IX., Experiments on the Resolution of *dl*-Benzylethylpropylisobutylsilicane Sulphonic Acid," by P. S. Kipping and H. Davies. "Synthesis of Diurea from Urea," by F. D. Chattaway. "Chlorine Derivatives of Substituted Ureas," by F. D. Chattaway and D. F. S. Wünsch. "Chemical Examination of Eriodictyon," by F. Tutin and H. W. B. Clewer. "Hydration of Precipitates," by S. U. Pickering. "Relationship between the Constitution and the Absorption Spectra of Pyridine and various Derivatives," by J. E. Purvis. "Formation of Cyclohexanone Derivatives" and "Action of Mustard Oils on the Ethyl Esters of Malonic and Cyanoacetic Acids," by S. Ruhemann. "Studies of Dynamic Isomerism Part VIII., The Relationship between Absorption Spectra and Isomeric Change, Absorption Spectra of Halogen, Nitro-, and Methyl-Derivatives of Camphor," by T. M. Lowry and C. H. Desch. "Interaction of Hydrogen and Chlorine," by D. L. Chapman and P. S. MacMahon. "Chloride of Nitrogen," by D. L. Chapman and L. Vodden. "Atmospheric Oxidation of β -Methylhydrindone," by A. H. Salway and F. S. Kipping. "Mechanism of the Reduction of Nitro-anilines and Nitrophenols" and "Relation between the Strength of Acids and Bases and the Quantitative Distribution of Affinity in the Molecule," by B. Flürscheim. "A Glucoside from *Tephrosia purpurea*," by G. Clarke, jun., and S. C. Banerjee. "Constitution of the Carboxylic Group" and "Relation between the Chemical Constitution and Optical Properties of the Aromatic α - and γ -Diketones," by Miss I. Smedley.

FRIDAY, 22nd.—Royal Institution, 9. "The World of Life, as Visualised and Interpreted by Darwinism," by Alfred R. Wallace, F.R.S., &c.

— Physical, 5. "Effective Resistance and Inductance of a Concentric Main, and Methods of Computing the Ber and Bei and Allied Functions," by A. Russell. "Luminous Efficiency of a Black Body" and "Use of the Potentiometer on Alternate Current Circuits," by C. V. Drysdale.

SATURDAY, 23rd.—Royal Institution, 3. "The Critical Faculty," by Prof. Sir Hubert von Herkomer, C.V.O., &c.

THE CHEMICAL NEWS.

VOL XCIX., No. 2565.

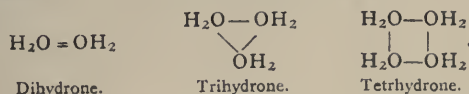
THE NATURE OF CHEMICAL CHANGE.*

By HENRY E. ARMSTRONG.

(Concluded from p. 30).

IT has been the great merit of the ionic dissociation hypothesis that it appeared to furnish an explanation of the fact that the active mass of a substance is always some fraction of the total mass. The fact that different acids have different degrees of hydrolytic activity, for example, is supposed to be due to the circumstance that at any given moment only that part of the acid is active which exists in solution in the form of dissociated ions—hence the supposed degree of dissociation has been regarded as the measure of activity. Until an alternative is offered such an explanation must prove attractive to those who cannot live without an imposed faith. The work which has been carried out under my supervision during several years past has, I think, made it possible to propound an explanation which is both rational and reasonable and generally applicable to the phenomena afforded by solutions. The subject is dealt with in a recent communication to the Royal Society (*Proc. Roy. Soc.*, 1908, Series A, vol. lxxxi., pp. 80—95).

I assume that water is a complex material and propose to confine the name to the liquid mixture. The simple molecule which we represent by the formula OH_2 I would term *hydrone*. Together with such monads there are present in water more complex molecules such as—



And most important of all perhaps are molecules of another type, represented by the formula $\text{H}_2\text{O} < \text{OH}^{\text{H}}$ —which I term *hydronol*. I will not stay to discuss the manner in which such molecules are formed—whether they could arise in pure water, such a substance being only conceivable, not obtainable.†

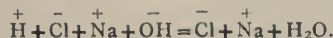
When a substance, hydrogen chloride, for example, is dissolved in water, it in part becomes *hydronated* and in part *hydrolated*, compounds such as $\text{HCl} = \text{OH}_2$ and $\text{HCl} < \text{OH}^{\text{H}}$ and polymerides of like type being formed; but another part is *hydrolysed* and converted into the compound represented by the formula $\text{H}_2\text{O} < \text{Cl}^{\text{H}}$, which is the correlative of hydronol. Compounds such as alcohol, which escape hydrolysis and only become hydronated and hydrolated, do not yield conducting solutions: it is only in cases in which both solvent and solute become re-distributed that conducting solutions are obtained—conduction being in some way dependent on the interaction of the two types of molecules $\text{H}_2\text{O} < \text{Cl}^{\text{H}}$ and $\text{HO} > \text{Cl}^{\text{H}}$ under the influence of the current.

This, I believe, is the first rational explanation that has been given of the nature of a composite electrolyte and is in agreement with the view expressed by Faraday that the determining force is not at the poles but within the body under decomposition.

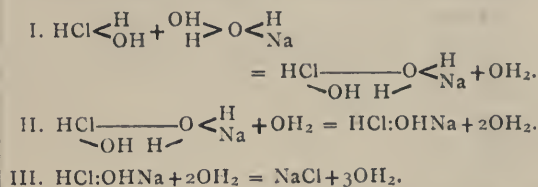
Subject to certain reservations the polyhydrones and all such compounds are to be regarded as inactive, being com-

pounds of tetrad oxygen; the activity of the solution is practically dependent on the proportion of molecules present either in the monadic or in the hydrolated or the hydrolysed state.

To give two illustrations of the application of the hypothesis. According to the dissociationists, when an acid is neutralised by an alkali, the only change within the liquid consists in the formation of water from the hydrogen and hydroxyl ions, e.g.,—



Unfortunately for this explanation, after full allowance is made for the water produced in the manner shown, it is still necessary to account for an expansion in volume corresponding to the formation of more than another molecular proportion of water. This difficulty disappears if the interaction be represented in the following manner:—



The proportion of hydrol actually set free and the amount of water formed (I. and II.) will depend on the amount of associated hydrol in the effective composite molecules of acid and alkali together with the molecular proportion liberated in the final change (III.), less the amount effectively associated with the dissolved salt—at most, two molecular proportions, therefore.

The volume changes are interesting from this point of view when determined in a series of solutions containing the same molecular proportions of solute and water—not in kilogram-normal solutions, the plan adopted by Ostwald.

TABLE II.—Volume of Weight-normal Molecular Solutions at 25°.

	Cc.	Ostwald.
KOH	1014.68	
NaOH	1001.28	
HCl	1021.98	
HNO ₃	1033.25	
Water (1000 grms.)	1002.97	
(KOH) + (HCl) = 2036.66 - 2005.94	30.72	
KCl = 1031.92 + H ₂ O = 1049.97 - 1002.97	47.00	
(18.05 cc.)		
Expansion	16.28	19.52
NaOH + HCl = 2023.26 - 2005.94	17.32	
NaCl = 1021.61 + H ₂ O = 1039.66 - 1002.97	36.69	
Expansion	19.37	20.05
KOH + HNO ₃ = 2047.93 - 2005.94	41.99	
KNO ₃ = 1043.48 + H ₂ O = 1061.53 - 1002.97	58.56	
Expansion	16.57	19.24
NaOH + HNO ₃ = 2034.53 - 2005.94	28.59	
NaNO ₃ = 1033.22 + H ₂ O = 1051.27 - 1002.97	48.30	
Expansion	19.71	19.77

The contraction observed when acids are neutralised by ammonia, which is especially large in the case of weak acids, is accounted for on the assumption that the amount of water fixed by the salt is large in proportion to that liberated from acid and alkali.

It is important, as far as possible, to avoid the use of "terminological inexactitudes" in describing the phenomena of chemical change. The word "ions" was introduced by Faraday simply "to express those bodies which can pass to the electrodes"; no thought of their freedom appears to have been in his mind: indeed it may be

* The introduction to a discussion on the subject in Section B (Chemistry) at the meeting in Dublin of the British Association for the Advancement of Science.

† I have discussed this subject somewhat fully in an article in the current number (January, 1909) of *Science Progress*.

claimed that he favoured the idea of association rather than that of dissociation (compare his fifth series of "Researches," §523). It is desirable to retain Faraday's definition of an ion unimpaired and to use the derivative terms ionised and ionisation only in a restricted sense: if we wish to imply that there is actual separation of the two constituent radicles, let us not be afraid to speak honestly of dissociated ions.

From the point of view here advocated, moreover, a particular substance should not be spoken of as ionised in solution but the solution should be said to be ionised—both constituents being reciprocally affected.

The assumption that both constituents of a solution—solvent and solute—take part in electrolysis is in accordance with the facts: for example, chlorine and hydrogen are practically the sole products only in the case of concentrated solutions of hydrogen chloride; as the solution is diluted, oxygen is obtained in increasing amount together with chlorine.

No proof has ever been given that conductivity is conditioned by the dissolved substance alone—the so-called molecular conductivities are merely a series of numbers expressing the conductivities of solutions of equivalent strength.

Weak and concentrated solutions must be regarded as containing very different proportions of the two kinds of active molecules: in the former, probably hydrolytated molecules of the solute of the form $HX \cdot \overset{H}{\underset{OH}{\text{O}}}$ are present in major proportion and, in some way, condition their superior activity as electrical conductors; in the case of concentrated solutions, hydrolysed molecules of the solute of the form $H_2O \cdot \overset{H}{\underset{X}{\text{O}}}$ are the major components and (in the case of acids and alkalis) the superior hydrolytic activity of such solutions is conditioned by these complexes.

The so-called osmotic properties and other physical attributes of solutions generally may all be regarded from the point of view now advocated but I may be allowed to refer to my recent communications to the Royal Society for an explanation of my views on this question.

The foregoing explanation of the condition of substances in solution should be considered apart from the question of the extent to which compounds are hydrated in solution. That hydrates are present is now generally admitted, even by those who advocate the ionic dissociation hypothesis in its extreme form; but apparently there is an unwillingness to allow that the hydrates which separate from a solution are to be regarded as having been present in it. Arrhenius, for example, in his Californian lectures, concludes an account of Meyerhoffer's observations on the freezing-points of solutions of sulphuric acid with the statement:—

"All these maxima and minima tell us nothing of the composition of the molecules in the liquid; they only indicate the composition of the substance which freezes out."

But it is in the highest degree probable that a substance which crystallises out from a solution is actually present in the solution prior to its separating: in other words, that the solid without is in equilibrium with the dissolved substance within the liquid in the case of a solution saturated in presence of the appropriate solid equilibrator. It is clear that the equilibrator has a determining influence in causing the separation of solid from the solution before this latter is actually saturated: the work of H. A. Miers and his coadjutors has shown, in fact, that if a solution be cooled in the absence of the appropriate equilibrator a point is reached at which the solution is actually saturated and solid then separates spontaneously, the temperature at which this separation takes place being often considerably lower than that at which crystallisation is effected in presence of an equilibrator. The mistake that has been made is that of assuming that a solution ever consists entirely of any one hydrate: probably, however, few have held this view in any strict sense. The existence of liquid crystals in solution may also be regarded as an argument in favour of the existence in solution as definite hydrates of substances such

as are known to separate in the solid state. But it is also conceivable that hydrates exist in solution of an indefinite character and that, in any case, the degree of hydration must vary with the conditions, not merely because the amount of water present varies but also because the condition of the water, the extent to which it is dissociated into hydrone, &c., varies with the concentration. It is to be supposed that in concentrated solutions, a major proportion is present in the form of hydrone and hydronol and that these will exercise a dehydrating and dehydrating effect (in other words, a dehydrating effect), owing to their tendency to become water; this tendency will be less manifest the weaker the solution; on the other hand, the interposition of a neutral substance, even though it be incapable of exercising directly any considerable dehydrating effect, may indirectly bring about a considerable amount of dehydration as a consequence of the dissociating influence which it exerts on the water with which it is mixed by promoting the occurrence of change in the direction $(OH_2)_x \rightarrow xOH_2$.

It may be doubted whether it will be possible to determine the exact degree of hydration of a substance in solution by any direct process: probably in every case only the average effect can be ascertained; the conditions in each particular system must be special, moreover.

The activity of acids as hydrolytic agents is increased, as a rule, if one of its salts be added to the solution of the acid: the concentrating effect thus exercised by the salt may be evaluated by determining the degree of dilution required to reduce the activity to that exercised by the acid alone. The hydration values thus arrived at, however, vary according to the nature of the hydrolyte. Thus, using gram-normal molecular solutions of hydrolyte and hydrolyst, the value arrived at for sodium nitrate by using nitric acid and cane-sugar is $11H_2O$, whereas if raffinose be substituted for cane-sugar the value falls to $8H_2O$, that arrived at by means of methylic acetate being still lower, viz., $3H_2O$. There can be no doubt that hydrolysis is a reciprocal process and that not only must the strength of the acid hydrolyst be taken into account but also that of the hydrolyte. Hydration values arrived at in the manner referred to cannot be regarded as true hydration values but merely as relative expressions of the degree of disturbance effected by the salt in the solution. Other methods of effecting such determinations are doubtless subject to similar limitations. It may well be that salts are actually more fully hydrated in solutions in which they apparently exert a minimum effect rather than in those in which they seem to act more powerfully.

Our mistake has been of late years that we have regarded the phenomena of solutions from too simple a point of view, especially that we have left the solvent out of account: in the long run, we shall be gainers if, as chemists, we allow the logic of facts to prevail.

ERRATUM.—P. 28, col. 1, line 31 from bottom, for "Paucity read "Sanity."

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South Kensington.

Products of Arc and Spark Discharge in Liquid Argon.—Franz Fischer and George Iliovici.—The authors have investigated the products obtained when liquid argon is subjected to arc and spark discharges between metallic electrodes in absence of air. Using cadmium electrodes they find that cadmium nitride is formed. The nitrogen of the nitride gives ammonium salts with acids, and escapes as N_2 when the nitride is ignited *in vacuo*. The gases which are obtained by heating *in vacuo* give in aluminium electrode tubes first the nitrogen spectrum and then the argon spectrum. Argon lines were at once obtained if the substance was opened up by the chemical union of the nitrogen with phosphoric acid. It appears that the argon is only absorbed, but the authors propose to perform further experiments with improved apparatus to decide this point.—*Berichte*, xli., No. 15.

THE CORROSION OF IRON.*

By ALLERTON S. CUSHMAN,
Assistant Director, Office of Public Roads, Dept. of Agriculture, U. S. A.

(Concluded from p. 34).

Application of Electrolytic Theory.

WE may now apply the electrolytic theory to the actual results obtained in the ordinary rusting of iron. If a section of rolled metal, such as sheet or plate, is immersed in water, if the electrolytic theory is correct, rusting must take place with the establishment of positive and negative spots or areas. At the positive points iron will pass into solution and be rapidly oxidised to the loose colloidal form of ferric hydroxide which is characteristic of rust formed under these conditions. It is a well known fact that colloidal ferric hydroxide will move or migrate to the negative pole if subjected to electrolysis. We may therefore consider the possibility of two separate effects that may be produced, viz., when a positive centre is surrounded by a negative area, and *vice versa*. These two conditions may be graphically represented by the two circles A and B shown in Fig. 3.

Now, as rusting proceeds we should expect in the case of A that the ferric hydroxide would be piled up in a crater formation, while the metal is eaten out at the centre. In the case of B the effect would be reversed, and while the

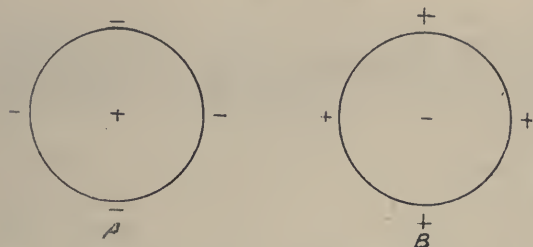


FIG. 3.—DIAGRAM ILLUSTRATING ELECTROLYTIC ACTION ON THE SURFACES OF IRON AND STEEL.

metal would be attacked in the surrounding area the hydroxide would be piled up in a cone at the centre. That this is precisely what is taking place whenever a sheet of metal rusts under water a low-power microscope very clearly shows.

The evidence advanced in the preceding pages appears to the writer to confirm the conclusion that the whole subject of the corrosion of iron is an electro-chemical one, which can be readily explained under the modern theory of solutions. It is an undeniable fact that some irons and steels suffer corrosion very much more rapidly than others, and the underlying causes for these differences constitute one of the most important problems of modern metallurgy.

Although the discussions brought forward in this bulletin are mainly theoretical in their nature, it is quite apparent that they also have an indirect practical bearing. Before advance can be made in overcoming the difficulties in the way of manufacturing iron which shall have the maximum resistance to corrosion, as well as the preservation of the metal under the conditions of service, the underlying causes must be thoroughly understood. If we accept the electro-chemical explanation of the corrosion of iron, there can be no doubt that conditions which inhibit electrolytic effects also inhibit corrosion, and *vice versa*. The purer the iron in respect to certain other metals which differ electro-chemically from iron and the more carefully lack of homogeneity and bad segregation are guarded against the less likely are the electrolytic effects to become serious. These points constitute the essential problems which confront the manufacturer who desires to make a product

which shall have a high resistance to corrosion. The user and consumer, however, are interested in the protection of the various types of merchantable iron and steel which are available under market conditions at the present time. In short, protective coatings and palliative methods of treatment are in greater demand to-day than ever before. From the standpoint of the electrolytic theory many suggestions for experiment under the conditions of service present themselves. The fact that hydroxyl ions inhibit the rusting of iron has been made practical use of for a long time past, and it is not unusual to add caustic alkalis to boiler waters for this reason. This, however, frequently causes trouble from foaming, and, as Cribb has shown (*loc. cit.*, p. 15), if an insufficient amount of alkali is present the pitting effect is accentuated rather than inhibited. This observation is in accord with the theory that the hydroxyl ions must reach a certain concentration, which varies with different conditions, before entire prohibition of the electrolytic effects is obtained.

At concentrations much below those necessary to prohibit electrolysis the action is similar to that obtained by adding a neutral electrolyte to the water, i.e., the electrolytic effects are localised if not stimulated. There should be many cases, however, where the property of alkalis to inhibit corrosion could be made of more practical use than has been done. Whenever iron posts or standards are set directly in the ground instead of being embedded in concrete, the liberal use of slaked lime should be beneficial.

The expedient of using metallic zinc in boilers to overcome the local electrolytic effects in the iron by producing a still greater electrolytic effect at the almost exclusive expense of the more positive zinc is well known and has been in use for a long time. Although the theory on which the use of zinc for this purpose is based is sound, great difficulty has been encountered in maintaining good metallic contacts between sufficiently large surfaces of the two metals under the conditions which maintain in a boiler. From what has been shown in regard to the inhibitive action of the chromates it is not improbable, since such dilute solutions prevent electrolysis and corrosion, that the addition of small quantities of bichromate to boiler waters would be highly efficacious in preventing the rapid pitting which has caused so much trouble. It has lately been reported that steel boiler tubes used on vessels fitted with turbine engines suffered corrosion to the point of failure in from two to four months' service (*Eng. News*, 1907, lvii., 426). This was found to be due to the fact that the steam, containing perhaps volatile acids, impinging on the bronze turbine blade, carried copper into solution and through the condensers into the boiler. Since iron does not change places with copper in dilute solution containing bichromate, it is possible that here again this salt would be found of practical value. That this statement is correct can easily be shown. If a bright piece of iron is immersed in a solution of copper sulphate so dilute as to show only a faint bluish tinge, the iron will nevertheless turn dark from precipitated copper in a very few moments. If now potassium bichromate is added in only just sufficient amount to give a yellowish instead of a bluish tinge to the solution, iron will remain bright and copper will not be deposited.

The experiment has been made by the writer of keeping iron and steel in dilute boiling solutions of bichromate for protracted periods at the same time that a current of air was bubbling through the boiler, and as long as the strength of the solution was equal to or above one-one hundred and sixtieth normal no rusting has ever taken place. Since this strength is approximately equivalent to one pound of the salt in 1500 gallons of water, there seems to be no reason why potassium bichromate should not come into use as a boiler protective. The application of the various inhibitors in the priming coats of paints and other protective coverings has already been to some extent made use of, and it would appear that slightly soluble chromates should be theoretically the best protectives for the first application to iron and steel surfaces.

* Bulletin No. 30, U. S. Department of Agriculture, Office of Public Roads.

A very widespread impression prevails that charcoal iron and puddled wrought-iron are more resistant to corrosion than steel manufactured by the Bessemer and open-hearth processes. It is by no means certain that this is invariably the case, but it would follow from the electrolytic theory that in order to have the highest resistance to corrosion a metal should either be as free as possible from certain impurities, such as manganese, or should be so homogeneous as not to retain localised positive and negative nodes for a long time without change. Under the first condition the irons would seem to have the advantage, but under the second much would depend upon care exercised in manufacture, whatever process was used.

The evidence appears to be conclusive that the corrosion of iron in all its forms is primarily due to hydrogen ions. The ability of various samples to resist the attack of an acid of a standard strength may turn out to bear some relation to resistance to corrosion under service conditions. A great variation in resistance to acid corrosion is shown by different specimens of both iron and steel. An investigation of this subject is being made in connection with the work of Committee U of the American Society for Testing Materials. Carelessly made and poorly segregated metal will be easily attacked, no matter what it may be called or what method was used in its manufacture. As has already been pointed out, there are two lines of advance by which we may hope to meet the difficulties attendant upon rapid corrosion. One is by the manufacture of better metal, and the other is by the use of inhibitors and protective coverings. Although it is true that laboratory tests are frequently unsuccessful in imitating the conditions in service, it nevertheless appears that chromic acid and its salts should under certain circumstances come into use to inhibit extremely rapid corrosion by electrolysis.

THE THERMO-CHEMISTRY OF PHOSPHORUS.

By J. C. THOMLINSON, B.Sc.

AMONG the data from which I contributed an article on this subject in the CHEMICAL NEWS (vol. xcv., p.), are given the following for the two allotropic forms of phosphorus, P_2O_5 :—

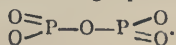
	Thermal value (cals.).
Ordinary yellow phosphorus	369·900
Red phosphorus produced by heating ordinary to 580°	326·860
Ordinary red phosphorus	362·820
Red phosphorus produced by heating ordinary to 360°	345·340

The heat of combustion of ordinary yellow and red phosphorus are approximately the same, the average of the two being 365·910 cals.

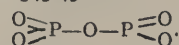
In that article I consider that phosphorus behaving as a quadrivalent element would have a heat of combination $P \equiv = 32·025$ cals., and oxygen as a monovalent element $71·228$ cals., when di-valent $52·545$ cals.

Applied to the two special cases of phosphorus undergoing allotropic modification at definite temperatures, we may arrive at some conclusion as to how these values for valency and the combining powers (heats of combination) of the elements may be applied to the mechanism of chemical change.

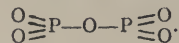
I propose to consider phosphorus as taking a quadrivalent part in combustion, and oxygen as having a variable valency in the cases given. In the combustion of ordinary red and yellow phosphorus representing three atoms of oxygen as di-valent, and two as mono-valent, we get a calculated heat of combustion, $364·141$ cals., the experimental value as given above being $365·910$ cals., the whole reaction of combustion being represented by the formula—



The modification prepared at 360° gives a heat of combustion $345·340$ cals., and representing the reaction in a similar way by the following formula we obtain a calculated heat of combustion $345·458$ cals.—



Finally, in red phosphorus prepared at 580° the heat of combustion is $326·860$ cals., and with the slight departure from the above of regarding phosphorus as pentavalent (*vide* vol. xcv.), $P \equiv = 31·340$ cals., and oxygen as di-valent, we get a calculated heat of combustion $327·405$ cals.—



The above formulæ represent the process of chemical reaction, as, of course, the final product phosphorus pentoxide is the same in each case.

January 7, 1909.

THE OSMOTIC PRESSURE OF CONCENTRATED SOLUTIONS, AND THE LAWS OF THE PERFECT SOLUTION.*

By GILBERT NEWTON LEWIS.

THE laws of the infinitely dilute solution have been thoroughly established. There can be no reasonable doubt as to the accuracy of Henry's law for the vapour pressure of the solute, Raoult's law for the vapour pressure of the solvent, or van 't Hoff's law for the osmotic pressure, in the case of an infinitely dilute solution. In fact, if any one of these laws is shown to be correct, the other two must follow as a direct consequence of the laws of thermodynamics.

Unfortunately, we never work with an infinitely dilute solution, and too little attention has been given to the question of the validity or even the mutual compatibility of the laws just mentioned in concentrated solutions and even in the so-called dilute solutions.

There is a well known thermodynamic relation between the osmotic pressure of a solution and the lowering of the vapour pressure of the solvent, which enables us, in every case, regardless of the concentration of the solution, to calculate the osmotic pressure when the vapour pressure lowering is known, and *vice versa*. It is therefore possible to calculate the osmotic pressure of a given solution, first, on the assumption that van 't Hoff's law† is correct, and second on the assumption that Raoult's law‡ is correct. It is commonly supposed that for fairly dilute solutions these two methods of calculating the osmotic pressure give identical results, but this is not the case. For example, the osmotic pressures calculated in these two ways for a normal solution of cane-sugar differ by 20 per cent, and even at the dilution of 0·005 normal the difference is still 0·1 per cent. It is obvious, therefore, that even in that region to which we are accustomed to apply the term "dilute solution," the law of Raoult and the law of van 't Hoff are not compatible. If one is true, the other must be false. What then shall we regard as an ideal or perfect solution; one that obeys the law of Raoult or one that obeys the law of van 't Hoff, or shall we choose another criterion which differs from both of these?

Morse and Frazier (*Am. Chem. Journ.*, 1905, xxxiv., 1; xxxvii., 324, 425, 558; 1907, xxxviii., 175), who have recently succeeded in measuring osmotic pressures up to 25 atmospheres by a direct method, propose to replace the law of

* From the *Journal of the American Chemical Society*, xxx., No. 5.
† $\Pi = nRT/V$, where Π is the osmotic pressure, R the gas constant. T the absolute temperature, and n is the number of mols. of solute dissolved in the volume V of the solution.

‡ $(p_0 - p)/p_0 = n_1/(n + n_1)$, where p_0 is the vapour pressure of the solvent in the pure state, p that of the solvent from the solution, and n_1 is the number of mols. of solute dissolved in n mols. of solvent.

van 't Hoff by the following equation, which gives values for the osmotic pressure more in accord with those obtained experimentally in the case of sugar and glucose:—

$$\Pi = \frac{nRT}{V'}$$

Here V' is not the volume of solution but the volume of pure solvent in which n mols. of solute are dissolved. These authors propose, therefore, to substitute for the system in which concentrations are expressed in mols. of solute in one litre of solution (volume normal system) another in which concentrations are expressed in mols. of solute dissolved in one litre of pure solvent (weight normal system). In most cases the difference between these two systems is much less than it is in the case of the two substances of high molecular weight investigated by Morse and Frazer. Thus a weight normal solution of sugar is only 0.82 volume normal, a difference of about 20 per cent, but in the case of methyl alcohol, ammonia, and hydrochloric acid, substances of small molecular weight selected at random for this calculation, the difference in concentration of weight normal and volume normal amounts to only 2, 4, and 2 per cent respectively. It is fortunate, however, that they did study those very substances in which the difference between the two systems is most pronounced, for we are thus forced to face certain questions concerning moderately dilute solutions which have been too often evaded.

It will be the purpose of this paper not only to find what theoretical justification there may be for the above modification of the van 't Hoff equation, but also to determine in general which of the various laws of solutions may be most suitably chosen to define the perfect solution.

Before beginning this inquiry it may be well to discuss briefly another question raised by Morse and Frazer, who write with some disparagement of the methods of determining osmotic pressure which rest upon thermodynamic calculations. Without undervaluing in any degree the importance of direct measurements of a quantity which has played so important a part in the development of modern chemistry as osmotic pressure, it must nevertheless be definitely affirmed that we have at our disposal several means of determining the osmotic pressure which are readily capable of furnishing results many times as accurate as any yet obtained by direct measurement. These methods will, therefore, be briefly considered in the following section:—

Direct and Indirect Osmotic Pressure Measurements.

The exact definition of osmotic pressure, and some of the thermodynamic relations in which the osmotic pressure is involved will be discussed briefly in notes at the end of this paper. There it will be shown that the osmotic pressure of an aqueous solution may be obtained at once from the freezing-point by means of the equation—

$$\Pi = 12.06\Delta - 0.021\Delta^2 \dots \dots \dots 1;$$

where Π is the osmotic pressure in atmospheres and Δ is the lowering of the freezing-point in centigrade degrees.

(NOTE.—If we assume that at infinite dilution van 't Hoff's law holds exactly, and take $R=0.08207$ litre atmospheres per degree, from the work of D. Berthelot (*Zeit. Elektrochem.*, 1904, x., 621), then we find from Equation 1 that the molecular lowering of the freezing-point of any aqueous solution at infinite dilution is 1.858° , which differs materially from the value commonly used, namely, 1.85° . The latter value is used by Morse and Frazer, but they should use the value 1.843 , for they do not employ the international atomic weights but those based on hydrogen as unity. The mol. is therefore reckoned in the latter system, and not in the customary one, in Tables I. and II. where Morse and Frazer's data are used).

From this equation the osmotic pressure of any solution up to ten or fifteen times normal may be obtained with an accuracy which depends only upon the precision of the freezing-point determinations and upon the accuracy of the

value used for the heat of fusion of ice. Since the error in the latter quantity is probably not more than about 0.1 per cent, it is obvious that, except for the most dilute solutions, osmotic pressures may be found in this way with an accuracy which is more than ten times as great as Morse and Frazer claim for their direct measurements. It is interesting to compare the osmotic pressures obtained by Morse and Frazer with those calculated by Equation 1 from the freezing-point measurement of the same authors. This comparison is made in Tables I. and II. The first column gives M , the number of mols. of solute in 1 litre of water, the second the lowering of the freezing-point, the third the osmotic pressure directly measured, the fourth that calculated from Δ , and the fifth gives in round numbers the percentage difference between the observed and calculated values. In Table I., I have also given (below the line) the osmotic pressure of cane-sugar solutions calculated from the freezing-point measurements of Ewan (*Zeit. Phys. Chem.*, 1899, xxxi., 22). These seem in perfect accord with the values of Morse and Frazer, and extend to higher concentrations. It is to be noted that each calculated value is obtained for the temperature at which the solution in question freezes, while the observed values were found at a few tenths of a degree above zero, but the correction for this small temperature difference is too small in comparison with the experimental errors to be considered.

TABLE I.—Cane-sugar.

M.	Δ .	Π obs.	Π calc.	Per cent difference.
0.1	0.195	2.44	2.35	4
0.2	0.392	4.80	4.73	1
0.3	0.585	7.16	7.05	2
0.4	0.784	9.40	9.45	1
0.5	0.985	11.8	11.8	0
0.6	1.19	14.2	14.3	1
0.7	1.39	16.8	16.7	0
0.8	1.62	19.3	19.5	1
0.9	1.83	22.1	22.0	0
1.0	2.07	24.8	24.9	0
0.867	1.77	—	21.3	—
1.25	2.68	—	32.2	—
1.54	3.42	—	41.0	—
1.63	3.63	—	43.5	—
2.10	4.88	—	58.4	—

TABLE II.—Glucose.

0.1	0.192	2.40	3.32	3
0.2	0.386	4.65	4.65	0
0.3	0.576	7.01	6.94	1
0.4	0.762	9.30	9.18	1
0.5	0.952	11.6	11.5	1
0.6	1.15	14.0	13.8	1
0.7	1.34	16.4	16.1	2
0.8	1.53	18.8	18.4	2
0.9	1.72	21.2	20.7	2
1.0	1.92	23.6	23.1	2

It is apparent that the observed and calculated values for the osmotic pressure agree within the limits of error of the former. The tables indicate, moreover, that the experiments with glucose were somewhat less reliable than those with cane-sugar.

Since, therefore, freezing-point measurements offer a simple and exact means of determining the osmotic pressure at the freezing-point, it is possible from them to determine the osmotic pressure at other temperatures, if we know its temperature coefficient. Morse and Frazer have considered it impossible to predict the value of this coefficient, but they have overlooked the simple thermodynamic equation, which may be derived immediately from the familiar energy equation of Helmholtz, namely,—

$$\Pi - q = T \frac{d\Pi}{dT} \dots \dots \dots 2;$$

where Π is the osmotic pressure, T the absolute tempera-

ture, and q is the heat of dilution; that is the heat evolved when 1 cc. of solvent is added to a large quantity of the solution. This quantity q is known for a large number of solutions, and in any case may be very easily determined. For cane-sugar we have very accurate knowledge of this quantity for one temperature, 15° , from the independent but entirely accordant work of von Stackelberg (*Zeit. Phys. Chem.*, 1898, xxvi., 533) and Ewan (*loc. cit.*). According to their measurements in the case of a weight normal solution q is equal to 0.12 cal. or 5 cc.-atmos. Substituting the latter value in Equation 2 and calling Π at 15° approximately 24 atmos., which according to the experiments of Morse and Frazer cannot be far wrong, we find—

$$\frac{d\Pi}{dT} = \frac{24 - 5}{273 + 15},$$

or about 0.07 atmos. per degree. In other words, while the osmotic pressure of an ideal solution at 15° changes 0.35 per cent per degree, the normal sugar solution changes only 0.27 per cent per degree. Unfortunately we do not know the heat of dilution of sugar solutions at lower temperatures, but since in other cases von Stackelberg has shown that it increases with decreasing temperature, it is probable that it does in this case also. The temperature coefficient of osmotic pressure will therefore probably become smaller at lower temperatures and may even become negative (when $q > \Pi$), which would explain the surprising fact discovered by Morse and Frazer that the osmotic pressure of cane-sugar is about the same at 0° as it is at 25° .

Since the heat of dilution may be very readily measured at any temperature, we have by its means a remarkably simple method of determining the osmotic pressure at any temperature, if it is known at one.

For obtaining the osmotic pressure of a solution at any temperature there is another perfectly general indirect method which has been frequently employed (see, for example, Noyes and Abbott, *Zeit. Phys. Chem.*, 1897, xxiii., 56) and recently has been improved to such a point that it rivals in accuracy the freezing-point method (see Smits, *Zeit. Phys. Chem.*, 1905, li., 33). It depends upon the thermodynamic relation between the vapour pressure from a solution and the osmotic pressure, which may be expressed in the equation (for the development of this equation, see Note 3, at the end of this paper)—

$$\Pi - \frac{1}{2} \alpha \Pi^2 = \frac{RT}{V_0} \ln \frac{p_0}{p} \dots \dots 3.$$

Here Π is again the osmotic pressure, α is the coefficient of compressibility of the solvent, V_0 is its molecular volume, $\ln$ stands for natural logarithm, and p_0 and p are respectively the vapour pressure of the solvent in the pure state and in the solution. Several applications of this equation will be made in the following section.

(To be continued).

A VOLUMETRIC METHOD FOR THE DETERMINATION OF BARIUM.

By ARTHUR E. HILL and WILLIAM A. H. ZINK.

Introduction.—Volumetric methods for the determination of barium appear to be few in number and somewhat limited in application. Sutton enumerates five methods in all, of which the best known is probably the direct titration of the barium compound in alkaline solution with standardised potassium dichromate until the supernatant liquid assumes a yellow colour ("Sutton's Volumetric Analysis," 1904, p. 161). The precipitate may also be filtered and washed, reduced by a measured excess of a ferrous salt, and the residual ferrous iron titrated with potassium permanganate (*Ibid.*, p. 162); see also Mohr, "Titrimethode," Braunschweig, 1886, p. 346). Barium hydroxide or carbonate may be titrated directly with

standardised acid (*Ibid.*, p. 69), while the neutral salts may either be titrated with sodium carbonate, using phenolphthalein as indicator (*Ibid.*, p. 69), or may be precipitated with ammonium hydroxide and carbonate and the washed barium carbonate titrated with standardised acid (*Ibid.*, p. 70). The new method here proposed depends upon the precipitation of barium as iodate and upon the oxidising action of this compound upon an iodide solution, with subsequent titration of the free iodine with sodium thiosulphate.

Discussion of the Method.—The solubility of barium iodate in pure water is given as 0.028 gm. of salt, or about 8 mgrms. of barium per 100 cc. of solution at 25° (Trantz and Anschütz, *Zeit. Phys. Chem.*, 1906, lvi., 238), an amount too large to admit treatment of the compound as an insoluble salt. In accordance with the theory of electrolytic dissociation, however, it might be expected that the solubility could be reduced to a negligible amount by the presence of a sufficient excess of a soluble iodate, provided that the barium iodate approximates complete dissociation when in saturated solution. A series of experiments showed that the desired condition is realised in neutral or alkaline solution when an excess of potassium iodate is used amounting to one-fiftieth formula weight per litre. Under these conditions the barium is so completely precipitated that 100 cc. of the filtrate show no turbidity upon being warmed with sulphuric acid. It was found that the solubility of the salt was increased slightly by the presence of other compounds, for which reason a concentration of iodate twice that stated above is recommended in carrying out the analysis.

The properties of the precipitated barium iodate are almost ideal for analytical work. It forms a white granular substance, settling quickly, and leaving a perfectly clear liquid above; the precipitation is complete within five minutes, if the mixture is well stirred. The granules are of sufficient size to filter easily without choking the paper, and a second filtration is but very rarely necessary. In these respects the compound is in marked contrast with other barium salts, such as the sulphate, carbonate (Knöfler, *Ann.*, 1885, ccxxx., 345), and chromate, or with the insoluble salts of the alkaline-earth metals as a class, which almost without exception are difficult to handle, require special precautions during the precipitation, and usually necessitate repeated filtration for their complete removal from the filtrate.

The critical point in the analysis of the barium iodate is its treatment after filtration. The precipitate cannot, of course, be washed with water, in which its solubility is far too great. Experiments were therefore conducted to ascertain whether a more suitable liquid for the washing could be found. Samples of freshly precipitated barium iodate were rotated at room temperature for twelve hours with the ordinary concentrated ammonia (sp. gr. 0.90) and with 95 per cent alcohol respectively, with the results which follow:—

	Ba per 100 cc Mgms.
Solubility of $\text{Ba}(\text{IO}_3)_2$ in 85 per cent alcohol..	3.1
Solubility of $\text{Ba}(\text{IO}_3)_2$ in concentrated NH_4OH	5.6
Solubility of $\text{Ba}(\text{IO}_3)_2$ in water (Trantz and Anschütz, <i>loc. cit.</i>)	8.0

Either concentrated ammonia or alcohol would therefore be preferable to water for washing purposes. It proved impossible, however, to make direct use of alcohol since it precipitates even the water-soluble iodates, which choke the filter-paper, and cannot be removed by a reasonable number of washings. A modified procedure has therefore been adopted; the precipitate is first washed a few times with concentrated ammonia, to remove the greater part of the excess iodate, and then finally subjected to several washings with alcohol. A series of test analyses was made to ascertain the extent to which this treatment might affect the accuracy of the results; constant quantities of barium chloride solution were precipitated with excess of potassium iodate, and the precipitates washed with varying

quantities of ammonium hydroxide and alcohol, and finally analysed according to the directions given later.

NH ₄ OH washings.	C ₂ H ₅ OH washings.	Ba taken. Mgrms.	Ba found. Mgrms.
2	3	84.40	84.40
3	3	84.40	84.42
4	6	84.40	84.49
5	3	84.40	84.24
8	3	84.40	83.81
3	8	84.40	84.03

The results indicate that the precipitate is not sensibly affected by being washed with ammonia from three to four times, or with alcohol from three to six times; when washed with ammonia five or more times, or with alcohol eight times, the precipitate loses slight but detectable amounts. In analysing barium solutions by this method it is therefore recommended to wash the precipitate three times with concentrated ammonia, and three to six times with 95 per cent alcohol.

In order to test this point still further, the ammoniacal and alcoholic washings have been tested for barium in over 150 analyses made in the course of this investigation. These washings averaged about 25 cc. of ammonia and 30 cc. of alcohol in each analysis, corresponding to about 8 cc. for each washing. The ammonia always contained slight traces of barium, which were estimated at from one-tenth to three-tenths of a mgrm.; the alcohol in many cases contained no barium that could be detected, and in a few cases traces that could hardly equal one-tenth of a mgrm. That the quantity of dissolved barium is less than its full solubility value in the respective solvents would be expected—first, because the potassium iodate used as precipitant is still in contact with the barium iodate during the washings with ammonia, reducing the solubility of the precipitate, and secondly, because granular and crystalline precipitates such as the barium iodate are often slow in reaching their solubility equilibria.

The method may best be described by the following specific directions for its use:—

Directions for Use of the Method.—The solutions required or the analysis are an approximately one-sixth normal solution of potassium iodate (about 36 grms. per litre) and a one-tenth normal solution of sodium thiosulphate, standardised by any of the usual methods, preferably against a known iodate solution. The soluble barium compound to be analysed is taken in an amount that will contain about 100 mgrms. of barium, brought into solution in a small beaker, and rendered neutral or faintly alkaline by addition of ammonium hydroxide, which should be free from carbonates. Water is added to make up the volume to about 60 to 70 cc. After calculating approximately the quantity of sixth-normal iodate solution necessary to precipitate the barium, add this quantity together with an excess of 25 cc., stirring the mixture well, and running in the iodate in a fine stream. Stir the mixture briskly for one minute, and allow it to stand, with frequent stirring, for five minutes longer. Filter through a 7 cm. filter-paper, used either dry or filled in the usual manner with water to which a little potassium iodate has been added. During the filtration avoid spattering the liquid on the sides of the funnel, so that the subsequent washing may not be rendered more troublesome. Catch the filtrate in a clean beaker, and use portions of the clear liquid in transferring the precipitate to the paper; use of a rubber-capped stirring-rod facilitates the operation. Wash the precipitate three times with concentrated ammonium hydroxide, filling the paper to its upper edge, and continue the washings three or four times with 95 per cent alcohol. Transfer the precipitate to a 500 cc. Erlenmeyer flask by perforating the paper and washing down the barium iodate with a stream of distilled water: finally add the washed filter-paper to the material in the flask. Add 50 cc. of a 10 per cent solution of potassium iodide, which has previously been treated with sodium amalgam or whose iodate content has been determined by a blank test. Add

10 cc. of concentrated hydrochloric acid solution, cover the flask, and allow it to stand, with occasional shaking, for five minutes. Wash down the sides of the flask and titrate the free iodine with the standardised thiosulphate solution, using starch as indicator. Each molecule of thiosulphate used corresponds to one-twelfth atom of barium.

The method as given above may be applied to solutions of barium as hydroxide, chloride, bromide, iodide, nitrate, and acetate, or other soluble salt of an organic acid. Sodium salts may be present in any amount, and magnesium, ammonium, or potassium salts in amounts up to one-half gm., calculated as chlorides. The modifications necessary when the latter salts are present in large amounts will be described in succeeding paragraphs.

The following analyses indicate the accuracy of the method when applied to pure barium compounds. They were made with a solution of barium chloride whose barium content was determined by gravimetric analysis, except in the case of No. 3, which was made with an analysed solution of barium hydroxide. The thiosulphate solution was standardised against an analysed potassium iodate solution. The potassium iodate (Kahlbaum's C. P. preparation) was analysed by reduction to iodide by means of a slight excess of sulphurous acid, the iodide precipitated with a slight excess of silver nitrate solution, and the silver iodide filtered on a Gooch crucible and dried to constant weight at 120°.

No.	Mgrms. Ba taken.	Mgrms. Ba found.	Error.
1.	34.24	34.22	-0.02
2.	34.24	34.20	-0.04
3.	61.14	61.20	+0.06
4.	85.84	85.83	-0.01
5.	85.84	85.72	-0.12
6.	120.08	120.15	+0.17

Effects of Foreign Bodies. Sodium Salts.—Analyses of a barium chloride solution to which were added quantities of a sodium chloride solution varying from one-half gm. to 3 grms. showed that no modification of the method is made necessary by the presence of sodium salts. When the sodium salt amounts to as much as 2 or 3 grms. special care should be taken to stir the solution vigorously and continuously during the precipitation of the barium iodate, which will otherwise carry down small quantities of sodium iodate, giving rise to high values for the barium.

Potassium Salts.—When present in amounts up to one-half gm., potassium chloride does not noticeably affect the accuracy of the barium determination. When present in larger amounts, however, it gives rise to values for the barium which may be 1 to 2 mgrms. high. The high values are probably due to the occlusion of potassium iodate. This salt can of course only be occluded from the undissociated portion of the compound, which is probably very small in quantity in the dilute solution from which the barium iodate is precipitated; when additional potassium salts are added, however, the dissociation is reduced and there is greater opportunity for the occlusion to occur. This occlusion can be prevented by carrying out the precipitation in hot solution. The faintly alkaline barium solution is heated nearly to boiling and the calculated excess of potassium iodate added in a thin stream, with constant stirring. The stirring should be continuous during the first one or two minutes, while the greater part of the precipitate is forming, after which the solution may be allowed to come slowly to room temperature or may even be cooled more quickly by immersion of the beaker in cold water. Frequent stirring is essential, whichever method of cooling be adopted, as small amounts of barium iodate will remain unprecipitated even after long standing, if the solution is left in quiet. When fully cooled, the mixture is filtered and the precipitate analysed as usual. Under the above conditions of precipitation the barium iodate forms a mass of gritty, glass-like crystals, whose rate of solution in hydrochloric acid is much slower than that of the softer and finer material formed by precipitation

in the cold. In order to avoid error from this source, the washed precipitate should be transferred to the Erlenmeyer flask with a rather small quantity of water, so as to avoid excessive dilution of the acid, and after addition of the potassium iodide and the hydrochloric acid the mixture should be shaken thoroughly until no particles of undissolved precipitate can be seen upon the bottom of the flask. Titration with thiosulphate before the oxidation of the iodide is complete is generally believed to give erroneous results. With the above modifications, the method may be applied to any mixture of barium and potassium salts. Analysis No. 4 in the following table was conducted in this way, while No. 3, in which only one-half gm. of potassium chloride was present, was carried out without this modification.

Ammonium Compounds.—Ammonium salts exert a slight solvent action upon the barium iodate, even when the acidity due to their hydrolysis has been overcome by addition of ammonium hydroxide, while the latter compound decreases the solubility of the barium salt, as solubility determinations have shown. Neither of these factors is of sufficient importance to affect the precipitation of the barium iodate measurably under the conditions of the method. It was found, however, that high results are obtained in the presence of large amounts of ammonium salts, just as with potassium salts, the compound occluded being presumably ammonium iodate. Precipitation from a hot solution, conducted as described in the preceding paragraph, reduces the occlusion below the limits of analytical detection, as shown by Analysis No. 8. When the amount of ammonium salt is less than one-half gm., calculated as chloride, the precipitation may be carried out in the cold; Analysis No. 7 was performed under these conditions.

Magnesium Salts.—Magnesium salts affect the method in the same way as potassium and ammonium salts. The precipitation may be carried out in the cold when the magnesium salt amounts to less than one-half gm., calculated as chloride; when the amount is larger, precipitation from hot solution is necessary. A small quantity of ammonium chloride should always be added to the solution to prevent precipitation of magnesium hydroxide when the solution is rendered alkaline, and more particularly to prevent formation of this compound and consequent choking of the filter when the precipitate is washed with concentrated ammonia. Analyses Nos. 9 and 10 illustrate the two methods of procedure.

Other Compounds.—Calcium and strontium must not be present in the solution except in traces, since their iodates are also precipitated in part under the conditions of the analysis. Tests in the presence of other metals were not conducted, since the iodates of nearly all the heavy metals are insoluble in alkaline solution. The method works without error in the presence of the various acid radicles mentioned previously.

The following table contains the results of specimen analyses conducted under the various conditions mentioned in the preceding text; they represent the average errors which occur when the barium solution contains other compounds. The solutions used in the analyses have been described previously.

No.	Compounds present.	Ba taken. Mgms.	Ba found. Mgms.	Error.
1.	0.5 gm. NaNO_3 ..	85.84	85.96	+0.12
2.	0.5 gm. $\text{NaC}_2\text{H}_3\text{O}_2$..	85.84	86.41	+0.57
3.	0.5 gm. KCl ..	85.84	85.95	+0.11
4.	3.0 grms. KCl ..	85.84	85.92	+0.08
5.	2.0 grms. NaCl ..	85.84	85.88	+0.04
6.	3.0 grms. NaCl ..	85.84	86.06	+0.22
7.	0.5 gm. NH_4Cl ..	85.84	85.44	-0.40
8.	2.0 grms. NH_4Cl ..	85.84	85.49	-0.35
9.	0.5 gm. MgCl_2 ..	85.84	85.96	+0.12
10.	2.0 grms. MgCl_2 ..	85.84	85.40	-0.44

On the basis of a fairly large number of analyses, conducted under widely divergent conditions, it may be

claimed that the method permits the determination of barium with an error not greater than a few tenths of a mgm. in the hundred; when pure barium salts are analysed, the error rarely amounts to more than a single tenth. The exceptional properties of the precipitate make the method of manipulation more convenient than any of the known volumetric methods. Two analyses can easily be conducted at the same time, and the average time required for their completion is about one hour and thirty minutes.—*Journal of the American Chemical Society*, xxxi., No. 1.

PROCEEDINGS OF SOCIETIES

SOCIETY OF CHEMICAL INDUSTRY. (LONDON SECTION).

Ordinary Meeting, January 4th, 1909.

Dr. J. LEWKOWITSCH in the Chair.

"Some Rarer Alkaloids of the Cinchona Group." By B. F. HOWARD, F.I.C., and O. CHICK.

The first part of the paper is taken up with a study of the use of cinchonamine hydrochloride as a reagent for the gravimetric estimation and detection of nitrates, making use of the peculiar property of this alkaloid in forming an insoluble nitrate. The method of estimation of nitrates gravimetrically is as follows:—A large excess of cinchonamine hydrochloride solution is added to the nitrate in solution, the mixture stirred, a little hydrochloric acid added, and allowed to stand for at least twelve hours. It is then filtered and washed with a minimum quantity of water, dried at 100° C., and weighed. This method was found to give good results in all cases in which it was tried, except in the case of nitrates of metals forming insoluble chlorides or oxychlorides. The second part describes determinations of specific rotation, molecular weight, and methoxy groups by Zeisel's method in the case of this alkaloid, and also cinchonidine, cupreine, quinine, and concusconine.

"A Physico-chemical Method for comparing the Antiseptic Value of Disinfectants." By Drs. S. B. SCHRYVER and R. LESSING.

The principle of the method consists in determining the inhibitory action of disinfectants on the rate of growth of bacteria, as measured by the rate of chemical change in the substrate. The latter consisted generally of a gelatin-peptone mixture, and the change was measured by determining the electrical conductivity. For this purpose a specially constructed pair of electrodes was employed. As the bacteria develop the gelatin is gradually broken down into albumoses, peptoses, amino-acids, and finally into ammonia and fatty acids. All these substances have a higher electrical conductivity than the original solution. Experiments were carried out with the object of correlating the chemical and physical changes in the substrate, and also of determining the influence of the age of any particular culture, when making a sub-culture into the same medium. It was found that if a sub-culture is made at an early stage of incubation, the rate of change produced in the substrate in the sub-culture was relatively slow; if made, however, during a period of vigorous growth, this change was rapid, and practically independent of the amount of inoculating fluid used in making the sub-culture. The effect of various disinfectants, both on fresh cultures and sub-cultures, was also investigated. By comparing the inhibitory effect of different substances, a measure could be obtained of their relative efficiency as disinfectants.

"Reactions between Dyes and Fibres." By W. P. DREAPER and A. WILSON.

Dyes which exhibit colour changes in the presence of

acids, such as methyl-orange or Congo-red, behave differently when dyed on fibres. On animal fibres this action is greatly retarded, and under some conditions is absent altogether. Increase of temperature may still further modify the normal reactions. On cellulose fibres the reactions are much the same as in aqueous solutions, but they are modified by the presence of neutral salts. These reactions indicate a closer relationship between animal fibres and dyes than in the case of fibres of vegetable origin. The colour changes which take place with most dyes in the presence of concentrated acids are also retarded in the presence of animal fibres with both acid and basic dyes.

FARADAY SOCIETY.

Ordinary Meeting, December 21st, 1908.

Dr. N. T. M. WILSMORE in the Chair.

MR. E. A. ASHCROFT, A.M.Inst.C.E., M.I.E.E., read a paper on "*The Influence of Cheap Electricity on Electrolytic and Electrothermal Industries.*"

The extent of future developments of electro-chemical industries will depend on the limits to which the cost of electric energy can be reduced at suitable sites. In most cases an industry only becomes economically possible when the price of power has been reduced below a certain point, which varies more or less for every electro-chemical industry. The author discusses, in particular, the lowest possible limits of cost for the production of electricity from water-power, with special reference to conditions such as exist to-day in Norway. Some industries (the smelting of iron, the manufacture of lime nitrogen, and the complete treatment of complex sulphide ores may be instanced), to be worked commercially, will require a supply of energy at a cost of about £2 per kw.-year, and this "low-grade limit" in the opinion of the author can only be obtained from what he calls water-powers of Class I., namely, those in which natural conditions enable the development and regulation of power at a very low expenditure of capital—of the order £7 per E.H.P. capacity, including all necessities up to the dynamo terminals. (The author estimates the corresponding figure at Niagara to have been not less than £30). The number of powers of Class I. are not very numerous, and their natural advantages will to some extent be neutralised by the values placed on the water-rights, but many examples exist, and the author gives full particulars of the cost of developing a concrete case in Norway of 7500 kw. capacity. This fall costs £7 8s. to develop and equip, and current can be sold at £2 10s. per kw.-year. It should be mentioned that at Meraker 3000 H.P. has been sold for £1 14s., and at Notodden (both in Norway) for £1 17s. per kw.-year. The second-best source of energy in bulk to-day is what the author calls waterfalls of Class II., namely, those where a high cost of regulation or development is necessary to bring the water to the place of consumption, and to ensure an even supply all the year round. From these electricity can be sold for about £5 6s. per kw.-year, while the corresponding figures for oil engines, gas engines, and steam engines are given by the author as £7 4s., £6 18s., and £8 6s. 6d. respectively.

Mr. W. R. COOPER (communicated) pointed out that the cost of water-power was frequently what it would fetch, and that it could not be likely to have a fixed value. The price of water-power tended to rise, that from other sources tended to fall; water-power should therefore be purchased outright by the consumers and not merely leased.

Mr. BERTRAM BLOUNT thought that the author had not done justice to sources of power other than water; the notion that very cheap power was required for all electro-chemical industries was erroneous. He referred to the possibilities of electric zinc smelting among the industries requiring cheap power awaiting development.

Mr. W. MURRAY MORRISON was also of opinion that

steam and gas power could be produced cheaper than stated by the author—the former, in some cases, for £3 per kw.-year. The author's Class II. water-power he considered a bad specimen, and he further criticised in some detail other figures given in the paper. He thought that not enough margin had been left for contingencies. The source of the capital was an important consideration that had not been discussed; on it frequently depended the nature and cost of labour. No two schemes were alike, and every one must be considered on its merits, taking all conditions into consideration.

Mr. L. GASTER pointed out that the Niagara plant had been designed for a far greater output than had up to the present been reached, and that therefore the limit of cost of production of power was far below the figures at present obtaining. He suggested the desirability of manufacturing such products as graphite and carborundum at European power centres.

Mr. CHARLES WEISS drew attention to the conditions under which the water-powers in the Bavarian highlands were being developed.

Dr. H. BORNs referred to some of the disadvantages of many water-powers, such as inconstancy of supply.

Prof. R. H. SMITH also remarked on the ice difficulty, which was of frequent occurrence. He did not think it possible, in the case of water-powers, to reach the low figures given by the author, and he took exception to the allowances for depreciation made in the paper.

Dr. E. FEILMANN suggested that very cheap power-gas schemes might be developed in connection with the peat-fuel industry, and he thought that large-scale experiments were being made in this direction.

Mr. E. A. ASHCROFT, in reply, said his principal purpose had been to draw attention to the very special kinds of water-power that were still available, although rare, and not to contrast the various modes of power production. His figures, to which he adhered, represented a probable average. The ice difficulties referred to did not exist in Norway.

THE RÖNTGEN SOCIETY.

ABOUT a year ago the Standards' Committee of the Röntgen Society, dealing with the problem of setting up a standard of radio-activity, recommended that the Gamma ray ionisation from 1 mgrm. of pure radium should be regarded as a standard and called a "unit of radio-activity." Mr. C. E. S. PHILLIPS, F.R.S.E., a member of the Committee, was entrusted with the task of sealing up some small quantities of radium to be used as sub-standards. At the meeting of the Society on January 7th last, Mr. Phillips read a paper on the subject, and formally presented three sub-standards containing between them about 0.5 mgrm. of RdBr_2 . The Röntgen Society intends to lend these sub-standards to competent people who require them for measurements of radium in their possession, and thereby to minimise the possibility of fraud in the sale of expensive radium preparations. The work of preparing and sealing up these standards, as described by Mr. Phillips, was one of considerable difficulty. In the first place, he obtained about 0.5 gm. of pure precipitated silica, and this he washed, sifted, and bottled. One mgrm. of radium bromide was then obtained and tested against a nearly pure specimen of known weight. It was dissolved in water, a small quantity of the prepared silica added, and on the liquid being evaporated the dry powder remaining consisted of silica particles coated with a layer of the radium bromide. The process was repeated with other small quantities of silica until scarcely any radio-activity could be detected from the inside of the vessel, and the silica was then mixed together and sealed into a glass tube. A carefully selected length of soda-glass capillary tubing was chosen for this purpose, and a small bulb blown at one end of it, the other end being shaped into a funnel. A spiral of thin platinum wire was intro-

duced into the tube to carry off any positive electrification, and the radium-coated silica was then dropped through the funnel into the bulb, after which the tube was exhausted and sealed off at the fine neck. After being subjected to prolonged annealing, the little bulbs were fitted into a suitable case and were ready for any of the purposes to which a standard might be put. In the course of the discussion, Mr. F. H. GLEW pointed out that Sir William Ramsay had recently made some experiments which tended to show that radium after a time appeared to lose its power to decompose water, and he (Mr. Glew) suggested that it would be well to have a standard of oxide of uranium kept just as jealously, and under the same conditions, as these radium standards. If, as might turn out to be the case, radium lost some of its properties more quickly than theory had predicted, there would at least be standards side by side with it with which comparisons could be made. Mr. PHILLIPS said that several radioactive standards had already been set up. There was one at Vienna, another in America, and there was also an oxide of uranium standard. He agreed that it would be interesting to bring them all into line. In reply to other questions, he said that before definitely weighing the radium in these sub-standards he intended to wait for three months until they had reached a radio-active equilibrium, when they would be compared with the known weight of radium at Victoria University, Manchester.

ROYAL SOCIETY OF NEW SOUTH WALES.

General Monthly Meeting, November 4th, 1908.

W. M. HAMLET, F.I.C., F.C.S., President, in the Chair.

THE following paper was read :—

"Note on Pucherite from West Australia." By E. GRIFFITHS, Caird Scholar, University of Sydney. (Communicated by J. A. SCHOFIELD, Acting Professor of Chemistry, University of Sydney).

The subject of this note was contained in a few grms. of concentrates from Niagara, W.A., forwarded by Mr. C. F. de J. Grut, M.A., B.E., of Kalgoorlie. It gave on analysis the following result :— Bi_2O_3 , 73.77; V_2O_5 , 25.31; Fe_2O_3 , 0.36; P_2O_5 , trace; residue (insol. in HCl) 0.81. The physical properties and composition of the mineral agree with those recorded in Dana's "System of Mineralogy" for the mineral Pucherite. This is believed to be the first recorded occurrence of pucherite in Australia.

Remarks were made by Mr. W. J. CLUNIES ROSS and the President.

Exhibits.

Mr. MAIDEN brought under notice of members the poisoning of human beings by a climbing plant known as *Rhus radicans* or "Poison Ivy," from North America, and occasionally found in gardens in New South Wales. It is a really dangerous plant, causing acute skin irritation, and a perfectly harmless plant, *Ampelopsis Veitchii*, is often mistaken for it. He showed how the two plants may be readily distinguished. "Poison Ivy" is far too poisonous a plant to be permitted in gardens, especially as it is not necessary to actually touch it to be affected by it. He also exhibited a plant of the beautiful *Primula obconica*, and showed a photograph to illustrate the very serious skin irritation induced in some persons who handle it. He explained that the irritating principle in the case of the *Primula* is the glandular hairs; in the case of the *Rhus*, known also as Poison Ivy, it is a peculiar oil.

A Discussion ensued in which the following gentlemen took part, viz.:—The President, Messrs. L. Hargrave, W. J. Clunies Ross, Dr. Spencer, Messrs. J. A. Schofield, L. Whitfield, H. G. Smith, and A. Duckworth.

Mr. J. H. MAIDEN replied, and promised to bring forward the matter of some other poisonous garden plants on some future occasion.

NOTICES OF BOOKS.

The Nature of Enzyme Action. By W. M. BAYLISS, D.Sc., F.R.S. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1908.

THIS volume is one of a series of monographs on biochemistry which is to be issued under the joint editorship of Professors R. H. Aders Plimmer and F. G. Hopkins. In this series the whole of the science is to be covered, so that when it is brought to a conclusion the monographs will constitute a complete treatise on the subject. The issue in different books has much to recommend it. The publication can be effected far quicker than if one large volume were to be prepared, and, moreover, as fresh editions become necessary they can be published without a re-issue of the whole series, so that the difficulty of keeping the series up-to-date is considerably diminished. In such a rapidly growing subject as chemical physiology the advantages of the plan are specially apparent, and it has been found to be most successful in the case of the series of Text-books of Physical Chemistry edited by Sir William Ramsay. Each monograph is to contain a bibliography, and is to be complete in itself. The first volumes of the series are to deal more especially with the general aspects of the subject, and with the pure chemistry of physiological products, while the subsequent books are to be devoted to the chemistry of special tissues. This, the first volume to come under our notice, treats in a very efficient manner of the enzymes—their chemical and physical properties, methods of preparation, &c.; details of the individual characteristics of specific enzymes are not included, the aim of the monograph being rather to supply a general review of the subject. The book is based upon lectures which were given by the author at University College, London; these, however, have been contracted in some directions and expanded in others, as seemed necessary for the issue in book-form. The author's own work on the nature and action of enzymes has led to some important advances in our knowledge, but he by no means gives prominence to his own views, and displays the utmost broadmindedness towards opinions which are in opposition to his own.

Cyanide Processes. By E. B. WILSON, E.M. Fourth Edition. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1908.

THIS book contains a very straightforward, simply worded account of the treatment of ore by the cyanide method, including the chemistry of the method, laboratory work necessary for testing the solutions employed, and a full description of the process. Detailed accounts of the machinery and apparatus are very wisely omitted, and the aim of the book is to give a clear presentment of the main features and principles of the process of cyaniding. In the fourth edition recent advances and improvements are described, special attention being devoted to the most modern methods of treating slimes.

Text-book of Physiological Chemistry. By EMIL ABDERHALDEN. Translated by WILLIAM T. HALL and GEORGE DEFREU. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1908.

THIS translation of a valuable German text-book on physiological chemistry must be at once recognised as a standard and authoritative text-book in which the most important results which have been obtained in physiological investigations are discussed in full detail. The first lectures deal with the three important classes of food substances, carbohydrates, fats, and albumins, first as regards their chemical composition, each class being treated separately. Their rôle and their metabolism in the organism are next discussed, and then their relations to one another and mutual replaceability are treated. The function and importance of inorganic foods is the subject of the following

ectures, and a short account is given of the nature and action of ferments. The functions of the digestive organs, the composition and character of the blood and lymph, and the quantitative study of metabolism are also discussed, and the two concluding lectures give a very clear and interesting survey more particularly of the problems which still remain to be solved. In these last chapters Ehrlich's side-chain theory, the outcome and true value of which can hardly yet be thoroughly realised, is given full consideration.

Practical Metallurgy. By THOMAS TURNER, M.Sc., A.R.S.M., F.I.C.. London: Charles Griffin and Co., Ltd. 1908.

In writing this book the author has had in mind more especially the requirements of candidates for the B.Sc. degree in metallurgy in the University of Birmingham; for this examination a three years' course after matriculation is necessary, and in the first two years the student has to work through a general introduction to the more specialised metallurgical work. This two years' course of practical work is covered in the book, which treats shortly of the analysis of alloys, clays, slags, ores, &c. No descriptions of the methods or apparatus of elementary chemistry are given, and thus there is the more room for technical matter. Each section is complete in itself, and there would be no difficulty whatever in making any desired alterations in the order in which the different branches are taken up. The exact details of each process are carefully described, and the student should be able to work successfully from the book with very little outside help. This, however, does not apply to the section on electrical work, which is discussed with extreme brevity, so that the consultation of other books would undoubtedly be found to be absolutely necessary.

The New Matriculation Chemistry. By G. H. BAILEY, D.Sc. (Lond.), Ph.D. (Heidelberg). Edited by WILLIAM BRIGGS, LL.D., M.A., B.Sc., F.C.S. Fourth Edition. London: University Tutorial Press, Ltd. 1908.

A FEW changes have been made in the fourth edition of the "Matriculation Chemistry," chiefly as regards the introductory section. This has been re-written by Mr. H. W. Bausor, M.A., and as it stands now provides the student with some training in practical work both qualitative and quantitative, while at the same time it gives him an insight into methods of scientific investigation. The outlines of chemical theory are also clearly treated in this section. The second part contains a systematic treatment of the non-metals and metals, and in the third part the chemistry of daily life is discussed, the syllabus of the matriculation examination being carefully followed. The book can safely be recommended for students, who may feel confident that no point in the syllabus has been neglected; indeed, in some cases for the sake of completeness extra subjects have been included. No reference book on chemistry will be needed by those who use this book, and as an elementary treatise for ordinary school use it will be found in many ways by no means inferior to the majority of such books.

Massing of Spheres. Part I. By G. J. STEVENS. London: J. Haslam and Co., Ltd. 1908.

In this pamphlet a rule or formula is given by which the exact atomic weights of all elements which can possibly exist are supposed to be obtained. By considering the structure of a compact mass of spheres it is found that in such a mass a series of measurements exists closely allied to the series of the atomic weights, and thus by triangulation it is possible to determine the dimensions of the elemental atoms, assuming that the radius of the ether sphere is unity. This process gives a succession of numbers which in some cases agree well with those representing the atomic weights of known elements. On the other hand, there are sometimes considerable discrepancies, and the scheme, ingenious

as it undoubtedly is, cannot by any means be described as convincing. The atomic weight of the ether is deduced to be 1, and it is thus commensurable with the elements.

Technical Chemists' Handbook. By GEORGE LUNGE, Ph.D., Dr.Ing. London: Gurney and Jackson. 1908.

THE German book of which this is a translation was originally intended for the use of alkali makers, and dealt only with the methods of analysis which are of special importance in alkali works. The latest German edition was extended to other important inorganic chemical industries, and the additional matter included the description of the analysis of the raw materials and products in the manufacture of fertilisers, the analysis of calcium carbide, acetylene, &c. The English translation of this latest edition is a valuable laboratory guide for technical chemists. In it only one method is given of estimating each constituent, so that its general use among chemists would be a step in the direction of establishing a standard of comparison accepted by all analysts. The first part of the book includes mathematical tables, tables of physical constants, and various mensuration formulæ, while in the second brief descriptions are given of the best methods of analysing the raw materials, lye, and final products of the chief inorganic chemical industries. No methods of analysing foods and feeding stuffs are given, but otherwise the book forms a complete practical text-book of all ordinary technical analytical processes.

Text-book of Physics. (Heat). By J. H. POYNTING, Sc.D., F.R.S., and J. J. THOMSON, M.A., F.R.S., Hon. Sc.D. (Dublin). Third Edition. London: Charles Griffin and Company, Ltd. 1908.

THIS text-book of physics is too well known to need recommendation, although it may not be amiss to point out some of its special features. Chief among these is the emphasis laid on experimental work, which is fully described and discussed, with in many cases clear diagrammatic illustrations. Moreover, examples of heat phenomena drawn from physiography are frequently instanced, while finally, none but the simplest mathematical processes are introduced, making the book specially suitable for students who have had only a very slight amount of training in mathematics. In the third edition a few mistakes which time and use have brought to light are corrected, and also some additions have been made relating chiefly to recent work.

Collection of Papers Contributed on the Occasion of the Celebration of Professor J. Sakurai's Jubilee. Tokyo: Reprinted from the *Journal of the College of Science.* 1908.

THIS collection of papers has been published in honour of the distinguished career of Prof. Joji Sakurai, of the University of Tokyo, who has made his name universally known as an original investigator, as a teacher, and as an author, more especially on subjects connected with physical chemistry. In addition, he has done much to promote educational and social reforms in Japan. The papers, written for the most part by his own pupils and describing researches carried out by them, form an admirable tribute to the inspiring and enthusiastic character of Prof. Sakurai's tutorial work. They are almost all published in English, the two exceptions being in German, and deal exclusively with chemical subjects. In every case a perfect lucidity of expression is displayed, and a very considerable command of the English language, any ambiguity or clumsiness of diction being altogether absent, though some misprints disfigure the articles in German. Possibly the papers which will attract the most attention are those describing the properties and preparation of the new elements which have been discovered in thorianite, reinitite, and molybdenite. The author of the paper, M. Ogawa, has isolated, firstly, an element of equivalent weight about 50, to which he has given the name "Nipponium (Np)," suggested by Sir William Ramsay; secondly, an element

closely allied to molybdenum and having an equivalent weight about 16.7; while there are also indications that thorianite contains yet another new element, the oxide of which is radio-active.

Water: its Origin and Use. By WILLIAM COLES-FINCH. London: Alston Rivers, Ltd. 1908.

THOSE teachers who think that a superficial knowledge of zoology and botany represents the best that is to be gained by "nature study" would do well to read this book written by an enthusiastic student of natural phenomena. As interesting as a novel and as instructive as a scientific treatise it may be said to rank as a romance dealing not with incidents or adventures, but with the development of character; it is a true character study of water. The water of the atmosphere, rain, snow, ice, springs, and wells are all discussed in a most interesting way, the chapters on the clouds and on glaciers being particularly delightful. Some account is given of different methods of obtaining water, the sinking of wells, the construction of water works, and the preparation of water for consumption for domestic purposes. The uses of water for irrigation and for working hydraulic machines are shortly discussed in the final chapter. To add to the charm of the book, it is illustrated by really beautiful pictures, those of mountain and glacier scenery having been reproduced from the originals of Mrs. Aubrey Le Blond. The author's hope that many who are not attracted by scientific works may find pleasure in this book we can sincerely echo, and add that the awakening of their interest in the wonders of nature through its instrumentality will undoubtedly be attended by genuine profit to themselves.

A Scientific View of Human Conduct. By GEORGE GORE, F.R.S., LL.D. Birmingham: Hudson and Woolston. 1908.

THIS pamphlet endeavours to prove the existence of a scientific basis of human conduct which is regulated strictly on the same mechanical and mathematical plan as controls inanimate nature. The essential differences between dogmas and scientific principles are explained, the value of the former being admitted as preliminaries to knowledge; thus they are looked upon as justified both by necessity and by their utility. Though the article contains no ideas of great novelty, yet possibly the truths are put forward in fresh aspects which will make them clearer to some readers, and the whole pamphlet is marked by a calm spirit of philosophical enquiry on a higher level and much more impressive than mere controversy. A short discussion of the reasons for the existence of pain and evil aims at showing that these are essential parts of the general scheme, acting in the direction of the good of the universe as a whole and not warring against it.

Les Densités des Solutions Sucrées à Différentes Températures. ("The Densities of Sugar Solutions at Different Temperatures"). By D. SIDERSKY. Brunswick: Friedr. Vieweg und Sohn. Paris: H. Dunod and E. Pinat. 1908.

THE existing tables connecting the densities of sugar solutions with the amount of dry extract exhibit many discrepancies among themselves, some being calculated for a temperature of 17.5°, and others for 15°, while German tables are referred to the density of water at 17.5° or 15° as unity, and French tables are based on the metric system. The correction for different temperatures is a matter of considerable complexity, and the deviations are often comparatively large. To remedy this state of affairs the author has calculated tables giving the dry extract of sugar solutions corresponding to densities observed at any temperature from 10° to 30°. An introduction giving a review of the different systems of tables in use is printed in two languages, the German text being on one page and the French opposite to it, and the book will undoubtedly be much appreciated by sugar chemists of both nationalities.

A B C Five-figure Logarithms. By C. J. WOODWARD, B.Sc. London: E. and F. N. Spon, Ltd.; Simpkin, Marshall, Hamilton, Kent, and Co., Ltd. New York: Spon and Chamberlain. Birmingham: Cornish Brothers, Ltd. 1909.

THIS little book of logarithms is wonderfully comprehensive and compact, and is well worth the price asked for it. Rules are given for using the tables, and these are so clearly stated that even the totally inexperienced will find no difficulty in performing all the ordinary operations with their help. The logarithms of arc functions are included, and many examples in crystallography, navigation, &c., are worked out. The lateral index, which enables the user to turn up at once any number he requires is a great convenience. A table of natural arc functions to each minute of angle has been added to the second edition, and on the covers indexes are given enabling the page on which a given logarithm of an arc function will be found to be determined rapidly.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvii., No. 25, December 21, 1908.

Synthesis of Ammonia by means of Peat.—H. Wolterreck.—When peat is treated as described in the author's previous communication (*Comptes Rendus*, cxlvi., 125), and the nitrogen is determined in the residue, it is observed that the percentage found is always greater than the amount present in the original peat, after four hours' treatment. After six hours' treatment, on the other hand, the amount is decreased to half the original quantity.

Humic Matter in Peat Moss.—L. Roger and E. Vulquin.—When peat is formed nitrogen and carbon accumulate in the degradation products of the plants. Neither pentosans nor hexosans are present in the humic matter. The alcoholic functions of the celluloses seem to persist, as shown by the formation of an acetylated compound and of a compound analogous to the thiocarbonate of cellulose. Several constituents of lignocellulose have been detected, an aromatic C₆ radicle and a secondary acetyl constituent CH₃CO. The unsaturated character of the latter is shown by the fixation of halogens. The humic matter also possesses acid properties.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Specific Heats of Gases.—(Reply to J. Hewett).—These have not been re-determined recently. Consult "Physico-Chemical Tables," by J. Castell-Evans, p. 526 *et seq.* (published by C. Griffin and Co.); also "Annuaire pour l'An 1908," pp. 533–537 (published by the Bureau des Longitudes).

MEETINGS FOR THE WEEK.

- MONDAY, 25th.—Royal Society of Arts, 8. (Cantor Lecture). "Public Supply of Electric Power in the United Kingdom," by G. L. Addenbrooke.
- TUESDAY, 26th.—Royal Institution, 3. "Albinism in Man," by Prof. Karl Pearson, F.R.S.
- WEDNESDAY, 27th.—Society of Dyers and Colourists, 8. "The Locust Bean and its Practical Application," by M. C. Lamb and F. J. Farrell. "Chlorinated Wool," by H. P. Pearson.
- Royal Society of Arts, 8. "The Part Played by Vermin in the Spread of Disease," by James Cantlie, M.A., &c.
- THURSDAY, 28th.—Royal Institution, 3. "Mysteries of Metals," by Prof. J. O. Arnold.
- Royal Society of Arts, 4.30. "Some Phases of Hinduism," by Krishna Gobinda Gupta.
- FRIDAY, 29th.—Royal Institution, 9. "Improvements in Production and Application of Gun-cotton and Nitro-glycerin," by Col. Sir Frederick L. Nathan, R.A.
- SATURDAY, 30th.—Royal Institution, 3. "Sight and Seeing," by Prof. Sir Hubert von Herkomer, C.V.O., &c.

THE CHEMICAL NEWS.

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THE NATURE OF THE α PARTICLE.

By Professor E. RUTHERFORD, F.R.S., and T. ROYDS, M.Sc.

THE nature of the α particle from radio-active substances has, for several years, been one of the most important questions in Radio-activity. The evidence as a whole indicates that the α particle is an atom of helium carrying a positive charge. Recent experiments of Rutherford and Geiger (*Proc. Roy. Soc.*, 1908) have substantiated this conclusion. An additional proof of the correctness of this point of view is afforded by the good agreement between the rate of production of helium calculated by Rutherford and Geiger, and the rate of production recently measured by Sir James Dewar (*Proc. Roy. Soc.*, 1908).

This evidence is, however, of too indirect a character to prove decisively that the α particle is an atom of helium. It might be possible, for example, that the expulsion of an α particle led to the liberation of helium from the active matter, but that the α particle itself was not an atom of helium. In order to give a definite proof of the identity of the α particle with a helium atom, it is necessary to show that helium can be obtained from accumulated α particles, quite independently of the active matter from which they are expelled. This has been done in the following way:—

Purified emanation, corresponding to the equilibrium amount from 150 mgrms. of radium, was compressed by raising a column of mercury into a fine glass tube about 1.5 cm. long. The walls of this glass tube were sufficiently strong to withstand atmospheric pressure but thin enough to allow the greater part of the expelled α particles to be fired through them. After a number of trials, Mr. Baumbach succeeded in blowing a number of such fine tubes for us. The emanation tube was surrounded by a larger cylindrical glass tube about 8 cm. long and 1.5 cm. diameter. This was first exhausted by a pump and the exhaustion completed by means of a charcoal tube immersed in liquid air. By means of another side tube connected with a mercury reservoir, the gases formed within the outside tube could be compressed into a small vacuum tube attached to the top and their spectra examined.

The tube containing emanation was about 1/100 mm. thick. The stopping power of the glass for the α particle corresponded to less than 2 cm. of air, so that the α particles expelled from the emanation itself, radium A and radium C escaped through the emanation tube, and were fired into the walls of the outer glass tube. Twenty-four hours after the introduction of the emanation, no trace of helium was detected on compression of the gases into the vacuum tube; at the end of two days the helium yellow line was seen faintly; after four days, the yellow and green lines came out brightly, and after six days practically the whole helium spectrum was observed.

An experiment was then made to test whether the helium observed could have diffused from the emanation through the thin glass walls. For this purpose, the emanation was replaced by about ten times its volume of helium and a new outer tube and vacuum tube placed in position. No trace of helium was observed in the outer tube over a period of eight days. Emanation was again introduced, and after four days the helium spectrum was again observed.

In these experiments every precaution was taken to prevent possible contamination of the apparatus with helium. Freshly distilled mercury and fresh glass apparatus was used. No trace of helium was observed unless the emanation was introduced into the fine capillary.

This experiment affords a conclusive proof that the α particle after losing its charge is an atom of helium. Other evidence indicates that the positive charge on the α particle is twice that carried by the hydrogen atom.—*Memoirs and Proceedings of the Manchester Literary and Philosophical Society*, vol. liii., Part I.

TANTALUM AND NIOBIUM IN AUSTRALIA.

By EDWARD S. SIMPSON, B.E., F.C.S.,
of the Geological Survey of Western Australia.

IN the census of minerals of Australia submitted to the Australasian Association for the Advancement of Science in 1890 no mention is made of any mineral containing tantalum and niobium. Since then, however, these rare metals have been recognised in several widely separated districts in the Commonwealth, and, in response to the recent commercial demand for tantalum ores, deposits of great richness and extent have been disclosed in the Pilbara Goldfield of Western Australia. In this paper an account will be given of the discovery of these interesting minerals in Australia, their mode of occurrence, and their chemical and physical characteristics.

General Features of Occurrence.

Before dealing with purely Australian deposits, it will be well to go briefly into the general features of the question.

These two metals are nowhere found in the native state, nor in sulphide or other similar minerals, but exist always in combination with oxygen and one or more other metals, the oxides having an acid character, and giving rise to tantalates and niobates. They invariably occur in conjunction, replacing one another isomorphously to a very variable extent, the niobate of a metal often passing by insensible gradations into the tantalate without change of form or physical characters other than a corresponding gradual rise in specific gravity, tantalum having an atomic weight double that of niobium. In this article, therefore, whenever a mineral is described as a tantalate it must be understood that it contains niobium as well as tantalum, but that the former is present in preponderating amount, and *vice versa*.

The ores hitherto detected in Australia are:—

1. Columbite, niobate of iron and manganese.
2. Tantalite, tantalate of iron and manganese. The subspecies manganotantalite contains more manganese than iron; the normal variety more iron than manganese.
3. Stibiotantalite, tantalate of antimony.
4. Microlite, tantalate of lime.
5. Euxenite, titanoniobate of yttrium, erbium, cerium, &c.

Until recently the best-known localities of the mineral tantalates and niobates were Sweden, Norway, Bavaria, Siberia, Greenland, and the United States. Though occasionally recorded as occurring in syenite rocks, the most usual primary occurrence in all these countries is in pegmatite veins in granite, especially in those characterised by the presence of much albite. In these veins they are commonly accompanied by quartz, orthoclase, and mica, as well as albite, whilst garnet, zircon, topaz, monazite, cassiterite, and other uncommon minerals are often present. The only primary deposits described so far in Australia are those of Finnis River, (Northern Territory), Greenbushes (Western Australia), and the Wodgina District (Western Australia), all areas of granitic rocks.

Most native tantalates and niobates offer considerable resistance to chemical change, and, being in the main both hard and tough, are of frequent occurrence in detrital deposits, though usually overlooked unless the latter happen to be worked for gold or tin. Still, there are numerous records of their detection in stream deposits in

America, Siberia, and England, whilst detrital ores are of great importance in North-Western Australia.

Within the last two years the search for these minerals has been greatly stimulated by the fact that they have suddenly become of considerable commercial value. This has been largely due to the discovery of the tantalum electric lamp, but partly also to the experiments being made with tantalum-steel alloys, which appear to possess many valuable properties. As much as 20s. per pound was paid in 1905 for bulk lots of high-grade tantalum ore. The price has, however, been very variable lately, ranging from about £200 to £1000 per ton.

QUEENSLAND.—Geraldton.—The only record of any tantalum in this State is contained in publication No. 196 of the Geological Survey. A black sand occurring on the shore at the mouth of the Johnstone River, near Geraldton, was found on analysis to consist mainly of ilmenite (84 per cent). With it was 0.78 per cent of combined niobic and tantalic oxides, equal to 0.95 of tantalite or columbite. Which of these latter minerals was present is doubtful, as no separation of the oxides was made. The only other rarer minerals present were monazite and zircon.

According to the 1902 geological map of Queensland, the watershed of the Johnstone River is occupied mainly by crystalline schists, with smaller areas of basalt. It is probably from the former—which may include granitic schists—or from offshoots of the large masses of granite lying further to the north and west, that the tantalite has been derived.

NEW SOUTH WALES.—Ballina.—In Vol. VII. of the Records of the Geological Survey of this State there is a description of some tantaliferous concentrates from Broken Head, near Ballina. The original beach sand from which these were obtained was composed of quartz, zircon, ilmenite, with smaller proportions of monazite, cassiterite, iridosmine, and gold. The concentrates consisted of:—Monazite, 65 per cent; zircon, 22 per cent; cassiterite, 9 per cent; and carried 1.10 per cent of tantalic oxide in one case and 0.86 in another, equal to between 1 per cent and 1½ per cent of tantalite.

Euriowie.—In the early nineties Mr. C. W. Marsh reported the occurrence of columbite in association with cassiterite at the Euriowie Tinfield, near Broken Hill. A small specimen of this columbite, about zin. long and ¾ in. square, is in the Geological Museum in Sydney. It is too small to permit of an exact analysis being made, and there is some slight doubt as to whether it may not be euxenite (niobate and titanate of yttrium, &c.). Its specific gravity is said to be about 6, which supports the theory that the mineral is columbite. The tin lodes at Euriowie, according to Mr. Pitman, consist of a series of coarse pegmatite dykes, traversing gneiss and mica schist. The dykes are described as being composed of quartz, felspar, and mica. It would be interesting to know whether the felspar is mainly orthoclase or albite, as the latter is so characteristic of tantaliferous dykes.

Silverton and Darling Range.—In a recent letter Mr. C. W. Marsh says:—"About two miles east of Silverton (Barrier Ranges) there is a large granitic outcrop, from which building stone has been quarried, having as accessory minerals tourmaline (black and red), ilmenite, garnets, and a little wolfram and columbite. I also remember finding columbite in granite at the southern point of the Darling Range, in the Rock Well Paddock, Barrier Ranges."

VICTORIA.—So far no tantalum or niobium is known to occur in this State. A mineral discovered some years ago, and reported to be columbite, proved on further examination to be rutile.

SOUTH AUSTRALIA.—As we leave the eastern side of Australia we find more frequent occurrences of these rare metals.

Boolcomatto and Mount Babbage.—In the previously quoted letter of Mr. C. W. Marsh, that gentleman gives the following particulars with regard to discoveries made by him apparently between 1885 and 1895:—"Sent from

Broken Hill to Boolcomatto, S.A., to inspect supposed important tin find, which turned out to be a large granite outcrop, containing as accessory minerals ilmenite and tourmaline, with a little wolfram and columbite. . . . Sent from Broken Hill to Mount Babbage, on the Northern end of the Flinders Ranges, S.A., to supposed valuable tin discovery, which turned out to be a deposit in creek bed consisting principally of dark garnets, with a little titanite and one large flat piece of columbite, with several small fragments of tantalite."

NORTHERN TERRITORY.—In a report on the north-western district of the Northern Territory by Messrs. H. Y. L. Brown and H. Basedow, recently published by the South Australian Government, a short description is given of the occurrence of tantalum ores in that region. Three localities are mentioned, all within 30 miles of Port Darwin, in tin-bearing country.

Finniss River.—This is apparently the only locality where tantalite is being raised for the market. The deposit was discovered twenty years ago, and worked for tin, the tantalite not being recognised as such until recently. As in so many other cases, it was—probably on account of its similar specific gravity—assumed to be identical with the tin ore which accompanied it. Messrs. Brown and Basedow described the deposit in the following terms:—"The ore-carrying body consists of a huge intrusion of greisen, trending south-westerly, with a slight underlie to the east. The outcrop measures from three to four chains in width, and about six chains in length. It is characterised by immense, compact, white inclusions of quartz. The texture of the matrix varies from abnormally coarse to sugary, the latter type of rock often containing epidote. Tantalite occurs practically throughout the mass, but is very erratic in its appearance as small bunches and isolated crystals. It assumes three modifications, depending largely upon the character of the enclosing matrix—firstly, as irregular inclusions in the compact white quartz, usually of a symmetrical outline or lamellar. In this form it occurs isolatedly, with no associated mineral. Secondly, as radial spherical crystal groupings in the rock of fine-grained texture. Thirdly, as regular rhombic crystal forms in a normal matrix, usually associated with tinstone. The country rock is an arenaceous mica schist. The main bulk of ore is obtained by surface work upon the decomposed dyke and its sheddings on the hill slope."

The ore in this locality is a mixture of cassiterite and mangano-tantalite, similar to that found at Wodgina, W.A., as shown by the following analyses taken from the report:—

	1.	2.
Tantallic oxide, Ta ₂ O ₅ ..	41.70	55.52
Niobic oxide, Nb ₂ O ₅ ..	19.00	24.92
Tin oxide, SnO ₂ ..	21.00	4.40
Manganese protoxide, MnO	14.83	11.16
Iron protoxide, FeO ..	2.14	2.73
Undetermined ..	1.33	1.27
	100.00	100.00

Bynoe Harbour.—Tantalum ore occurs as dyke diseminations on a mineral licence, nine miles south of the Leviathan Tin Mine, and also on Horden and Paull's claim, close to the other deposit.

Port Darwin.—Tantalum ore is described as occurring in a similar manner six miles east of King's Table, West Arm of Port Darwin.

WESTERN AUSTRALIA.—Moolyella.—This locality, ten miles north-east of Marble Bar, is chiefly of importance for the tin ores which are produced there. According to the report of Mr. A. Gibb Maitland the field lies in the midst of a large area of granite, which is intrusive into sedimentary rocks of probably Cambrian age. This granite is traversed by numerous dykes of a pegmatite composed mainly of quartz and albite, with subordinate mica, garnet, and cassiterite. Considerable quantities of stream tin are being obtained in this field, this ore being undoubtedly due to the disintegration of the pegmatite dykes.

In a parcel of stream tin ore in the museum of the Geological Survey of Western Australia is a single fragment of a mineral forming a quadrant of a sphere 1 in. in diameter, with radiated crystalline structure. This mineral is of an intense black colour, with a metallic lustre, and specific gravity 7·3. It is identical in appearance with some of the ore from Wodgina, and is without doubt manganotantalite. It is an aggregate of a number of wedge-shaped crystals, the mass parting readily along radial planes on being struck. Closely attached to its outer surface are numerous small fragments of quartz and several fragments of much altered albite. These indicate the original source of the mineral to have been those quartz-albite pegmatite veins which form the matrix of the cassiterite.

Another similar, but smaller, fragment occurs in a second sample of stream tin ore, and others still smaller may easily have been overlooked.

Cooglegong.—This tinfield occurs thirty miles to the south-west of Marble Bar. According to the researches of Mr. A. Gibb Maitland, it is situated in the midst of a large area of granite, which, in places, is gneissic. "The granite is intersected in certain localities by veins of pegmatite, which have doubtless been the original source from which the stream and residual tin have been derived."

Gadolinite has been found both in the stream deposits and, associated with cassiterite and monazite, in a pegmatite vein.

In a paper on this occurrence of gadolinite, read before the Royal Society of New South Wales, in October, 1902, Mr. B. F. Davis says:—"Amongst the minerals I brought from the north-west I have two varieties of a mineral allied to 'euxenite' in physical characteristics, as described by Dana. One differs from the other in having more manganese in the place of uranium. They are essentially niobates and titanates (with tantalum) of uranium iron and yttrium earths, with cerium earths and thorium. They occur with cassiterite and monazite in the wash-dirt. I have only a few small pieces, but one mineral at least was not uncommon. I saw it in all the tin ore bagged from different parts of the country."

Some of the mineral from this same locality, collected from samples of tin concentrates by Dr. McKenzie, of the Tin Smelting Works, Sydney, has been examined by Mr. D. Mawson, and found to be strongly radio-active.

It is not, however, at all clear from Mr. Davis's paper whether this mineral was really obtained at Cooglegong or not. It may possibly have come from Moolyella.

I have recently come across some specimens in the West Australian Museum, the locality of which is given as the Shaw River, so that they come either from Cooglegong or from the Old Shaw Tinfield a few miles out of Cooglegong. These specimens consist of a number of angular detrital fragments of typical euxenite, varying in size from 10 to 40 mm. in length, and coated externally with a brown clay. On a fresh fracture the mineral is brown in colour, and possesses a brilliant resinous lustre. It has a specific gravity of 5·3.

Thelemann's Find.—Sixteen miles north-west of Lalla Rookh tantalum ore was obtained in 1906 by Mr. F. Thelemann. It is detrital ore, and is said to occur only in limited quantities. It is of little commercial value, being a low-grade iron columbite, assaying from 3 per cent to 5 per cent of tantic oxide. One sample, consisting of more or less worn fragments from a quarter to 1 inch in diameter, contained 4·92 per cent of tantic oxide, 70·34 per cent of niobic oxide, and no tin. The specific gravity of the constituent fragments was very uniform, averaging 5·5.

The ore from this locality is frequently well crystallised. One good crystal measuring 7 × 23 × 30 mm., and having a specific gravity of 5·53, shows the following faces:—*a*, 100; *b*, 010; *c*, 001; *u*, 133; *e*, 021; *m*, 110; *g*, 130; *y*, 210. The lower half of this crystal has not developed, having apparently formed against an already crystallised mass of albite. Several other crystals, with fewer faces, have been collected from this locality. Many are not of

the tabular habit of the crystal described. All are, however, of low specific gravity, indicating a low tantalum content. One fragment has the radiated spherical structure previously mentioned in connection with Moolyella. The only associated minerals observed were quartz, tourmaline, and albite. Granite is the prevailing rock in the locality.

Green's Well.—The main workings in this district are situated at a locality variously known as Green's Well, Mount York, and Chingamong. They were first developed in 1905, and are situated in the same belt of granite as extends from Thelemann's Find through Wodgina to Mount Francisco.

The original mine in this locality has been described officially in the following terms:—"On M.L. 100 (O. T. Bell and party) a rubbly felspar formation has been exposed for a few feet. This carries tantalite, but sufficient work has not been done to allow of an opinion as to the richness of the lode. On McBeth's alluvial reward claim tantalite can be easily seen in the gully that traverses the claim."

A sample of dressed ore from Green's Well, brought to Perth by Mr. A. Gibb Maitland, apparently consists of both stream and lode ore in angular fragments from 1 up to 20 mm. in diameter. A great portion of it is more or less well crystallised, a few excellent crystals being observed in it, of which the following are details:—

No.	Size in millimetres.	Sp. gr.	Faces observed.
1.	6 × 9 × 16	6·31	<i>a</i> , <i>b</i> , <i>c</i> , <i>u</i> .
2.	3 × 10 × 11	5·30	<i>a</i> , <i>b</i> , <i>c</i> , <i>u</i> , <i>e</i> , <i>y</i> , <i>m</i> , <i>g</i> .
3.	6 × 10 × 13	6·49	<i>a</i> , <i>b</i> , <i>c</i> , <i>q</i> , <i>h</i> (?).
4.	7 × 9 × 18	6·05	<i>a</i> , <i>b</i> , <i>c</i> , <i>u</i> .
5.	7 × 7 × 12	6·32	<i>a</i> , <i>b</i> , <i>c</i> , <i>u</i> , <i>k</i> .
6.	11 × 19 × 26	5·77	<i>a</i> , <i>b</i> , <i>c</i> , <i>u</i> , <i>e</i> , <i>m</i> .

The sample, as a whole, assayed—tantic oxide, 42·39 per cent; niobic oxide, 21·09 per cent; metallic tin, 15·62 per cent. The mineral itself varies from a columbite, with specific gravity 5·35, to a tantalite, with specific gravity 6·84. For the most part it has a dull rusty-black surface, but occasional crystals exhibit brilliant black metallic faces, especially *a*. This face and *b* is often striated vertically. The only associated mineral observed in any abundance is cassiterite. The primary deposit from which the ore is derived appears from the above description to be a typical quartz-albite pegmatite.

The ore from Green's Well is characterised by the very variable extent to which tantalum and niobium replace one another. In another sample from here, individual crystals varied in specific gravity from 6·4 up to 7·7, indicating an approximate percentage of tantic oxide varying from 46 to 81.

Wodgina.—By far the most important tantalum deposits in Australia are those of Wodgina, situated in the Pilbara Goldfield, in lat. 21° 15' S., long. 118° 40' E., 90 tons of dressed ore having already been shipped from this locality.

In a recent article in the *Mining Journal*, Messrs. F. H. and W. A. Mitchell (the latter assayer at the Mons Cupri Copper Mine, 80 miles from Wodgina) make the following statement with regard to the first discovery of tantalum ore at Wodgina:—"This mineral was first observed by us in North-West Australia early in 1901, when a crystal was submitted to the British Museum authorities for confirmation; but it was not until about four years later that we introduced this mineral into Europe for commercial purposes."

In May, 1904, a black mineral from this locality was forwarded for identification to the Acting Mineralogist and Assayer, Mr. C. G. Gibson, and proved to be manganotantalite, a preliminary analysis showing the presence of 80 per cent of tantic and niobic oxides and 16 per cent of manganese oxide. At that time there was no market for the mineral except for museum and other educational purposes, for which purpose the demand was limited to a few pounds per annum. Towards the end of the year, however, the demand which arose in connection with the

manufacture of tantalum lamps stimulated prospecting for these minerals, and since then a great number of ores from all parts of the district have been examined in the laboratory attached to the Geological Survey of Western Australia.

The locality has recently been geologically examined and mapped by Mr. Maitland, and from his report the following *resumé* of the structural features of the rock masses and ore bodies has been culled.

The tantalum ores occur in stream deposits, in shallow surface detritus in the immediate vicinity of the outcrops of pegmatite dykes, and in these dykes themselves. They occur in a mass of hornblende-schist, and are apparently offshoots of a mass of granite lying at a short distance to the north, east, and south-east. Between the hornblende rock and the granite on the south-east are a series of schists of indeterminate origin, mostly very siliceous and carrying either mica or hæmatite. Their origin is still a matter of some speculation. Within the area of these schists the pegmatite veins are tin-bearing, and are being worked for that metal.

The most important tantalum vein in Wodgina proper is that which passes through mining leases 86 and 87 in a north and south direction. It is from 30 ft. to 40 ft. wide, and consists of variable proportions of quartz, feldspar (mainly albite), mica (muscovite and lepidolite), and tantalite; the last-named in crystalline masses from the size of shot up to 5 cwt. in weight. A little west of this main vein is a second smaller one of similar nature. From the outcrops of these veins a larger amount of ore has been shed, and the greater part of the ore hitherto exported has been obtained by "specking" and dryblowing the shallow detritus on the surface. About 71 tons is said to have been obtained in this way.

The main vein appears to continue for about a mile north, where it is 20 ft. wide, and has there also been worked for tantalum.

Since Mr. Maitland reported on this field other tantalum-bearing dykes have been opened up in the vicinity, and ore is still being obtained from shallow surface soils, as well as from true alluvial deposits in the many small valleys.

(To be continued).

THE OSMOTIC PRESSURE OF CONCENTRATED SOLUTIONS, AND THE LAWS OF THE PERFECT SOLUTION.*

By GILBERT NEWTON LEWIS.

(Continued from p. 42).

The Law of Ideal Solutions.

WHAT we shall call a perfect or ideal solution is somewhat a matter of choice. We might define as an ideal solution one which obeys the law of van't Hoff, or the modified form of this law proposed by Morse and Frazer, or the law of Raoult, or the law of Henry. These laws are essentially identical for the infinitely dilute solution, but for a solution of finite concentration we are at liberty to choose one but not all of these laws to define the ideal solution. No one of them is true for every solution at every concentration, and we must therefore choose that one which holds most nearly for the greatest number of substances over the widest limits of concentration.

I shall attempt to show that the most fundamental law of solutions and the one by which the perfect solution is best defined is the following modification of the law of Raoult. *At constant pressure and temperature the activity of the solvent in a perfect solution is proportional to its mol. fraction.* (For a definition of the term activity see Lewis, "Outlines of a New System of Thermodynamic

Chemistry," *Proc. Am. Acad.*, 1907, xliii., 259; and *Zeit. Phys. Chem.*, 1907, lxi., 129; *C. A.*, 1908, 611). That is—

$$\xi = \xi_0 N \dots\dots\dots 4;$$

where ξ is the activity of the solvent in the solution, ξ_0 the activity of the pure solvent, and N , the mol. fraction, is the number of mols. of solvent in one mol. altogether of solvent and solute. Since, however, the conception of activity is new, and since if the vapour of the solvent obeys the gas law the activity is proportional to the vapour pressure, we may with sufficient exactness for our present purposes, substitute the vapour pressure of the solvent for its activity and write—

$$p = p_0 N \dots\dots\dots 5;$$

that is, in a perfect solution the vapour pressure of the solvent is proportional to its mol. fraction. (The point of view here adopted is practically identical with that which for several years has been advocated by J. J. van Laar in numerous publications). Thus in a solution containing 0.1 mol. solute to 0.9 mol. solvent, $N = 0.9$ and the vapour pressure of the solvent should be nine-tenths of its vapour pressure in the pure state, or if the solution contains 0.25 mol. solute to 0.75 mol. solvent, p should be 0.75 p_0 . This is simply a statement of Raoult's law in its simplest form.

(NOTE.—It is important to note that Equation 4 leads us immediately to a simple equation for the activity or the vapour pressure of the solute. In the paper previously referred to I have proved the following exact equation for the change in the activity of each component of a binary mixture with change of composition, namely—

$$N_1 d \ln \xi_1 + N d \ln \xi = 0,$$

where N_1 is the mol. fraction and ξ_1 the activity of one constituent which we will call the solute, and N and ξ are the corresponding terms for the other constituent which we will call the solvent. Now, when Equation 4 is true, $d \ln \xi = d \ln N$. Substituting in the above equation and noting that by definition $N_1 = 1 - N$ we find—

$$N_1 d \ln \xi_1 + dN = 0, \text{ or}$$

$$d \ln \xi_1 = d \ln N_1, \text{ or}$$

$$\xi_1 = K N_1,$$

where K is a constant. We see, therefore, that in a perfect solution it is also true that the activity of the *solute* is proportional to its mol. fraction. If we substitute p_1 , the vapour pressure of the solute, for ξ_1 , $p_1 = K N_1$, which is, in a slightly modified form, the law of Henry. In other words, if both vapours obey the gas law, the law of Henry may be derived thermodynamically from the law of Raoult and must hold if that law does).

There are no cases in which the law of van't Hoff or the modified form of this law proposed by Morse and Frazer have been shown to hold at concentrations higher than normal. (In a normal solution in water the mol. fraction of the solute is about 0.02).

Indeed, at very high concentrations van't Hoff's law cannot hold, for the osmotic pressure of a solution approaches infinity as the percentage of solvent approaches zero, while the osmotic pressure calculated from the van't Hoff equation never exceeds a few hundred atmospheres even when we approach the condition of pure solute. On the other hand, it will be shown presently that the law proposed by Morse and Frazer ordinarily gives, at higher concentrations, osmotic pressures far higher than those which actually exist. But often the law of Raoult (and the modified law of Henry) has been shown to hold at all concentrations from 0 per cent to 100 per cent of solute, and while in many other cases this law does not hold, the greatest deviations are always found in those cases in which we have reason to believe that the solvent and the solute form complex compounds either with themselves or with each other.

Many illustrations might be given to show the remark-

* From the *Journal of the American Chemical Society*, xxx., No. 5.

able scope of Raoult's law. I will choose a binary mixture which has been studied more carefully over a wide range of concentration than any other, namely, benzene and ethylene chloride. The vapour pressures are taken from the excellent paper of Zawidzki (*Zeit. Phys. Chem.*, 1900, xxxv., 129). We will call benzene the solvent and ethylene chloride the solute. In Table III., in which the data marked by Zawieski as questionable are omitted, the first column gives the number of grms. of solute to 1 grm. of solvent, the second gives the partial vapour pressure of the solvent at 50°, and the third gives the molecular weight of ethylene chloride calculated from the vapour pressures by Raoult's law. The calculated molecular weights are constant, even up to the highest concentration, where the solute constitutes over 90 per cent of the solution. The average of these calculated molecular weights is 99.1, while the actual molecular weight of ethylene chloride is 99.0. (We have therefore every ground for believing that also in the pure state ethylene chloride exists in the form of simple molecules).

TABLE III.

Grms. $C_2H_4Cl_2$ to 1 grm. C_6H_6 .	p of C_6H_6 .	M.W. $C_2H_4Cl_2$.
0.0	268.0	—
0.525	189.8	99.4
0.904	156.0	98.2
1.39	127.8	98.7
2.43	92.4	99.3
3.89	65.9	99.0
14.54	21.8	100.0

Average 99.1
Theoretical 99.0

If then we define a perfect solution as one which obeys Raoult's law,* it is interesting to find what the law is connecting osmotic pressure and concentration in a perfect solution. This law, which is less simple than either the law of van't Hoff or that of Morse and Frazer, may be derived directly from Equations 3 and 5, and is—

$$\Pi - \frac{1}{2} a \Pi^2 = - \frac{RT}{V_0} \ln N \quad \dots \quad 6,$$

or—

$$\Pi - \frac{1}{2} a \Pi^2 = - \frac{RT}{V_0} \ln (1 - N) \quad \dots \quad 7,$$

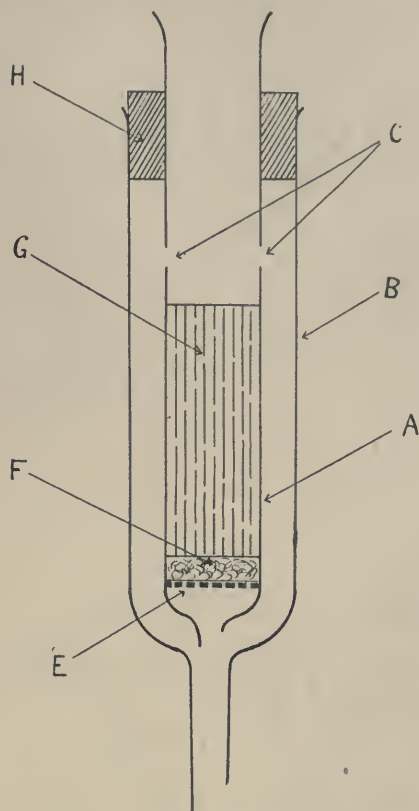
where V_0 is the molecular volume and a the compressibility of the solvent.

(To be continued).

AN APPARATUS FOR SIMULTANEOUSLY EXTRACTING A SOLID AND FILTERING THE SOLUTION SO OBTAINED.

By FREDERICK RECORD, B.Sc.

IN the CHEMICAL NEWS of June 12, 1908 (vol. xcvi., p. 280) there appeared a drawing and description of a form of apparatus for the above purpose, which consisted wholly of glass, and which had the disadvantage of requiring considerable skill in its construction. The accompanying section shows a modification of the apparatus which can be made much more readily. The inner tube, A, is contracted at its lower extremity, and has a pair of diametrically opposite holes, c, in its walls; it is held in position inside the outer tube, B, by means of a cork, H; E is a filter disc which is covered with a layer of filter-paper and



of asbestos, F; G is the substance to be extracted. The flask containing the solvent is attached to the lower end of B, while a reflux condenser is connected to the upper end of A.

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THE PRESENCE OF A CHOLESTEROL SUBSTANCE IN SOILS: AGROSTEROL.*

By OSWALD SCHREINER and EDMUND C. SHOREY.

IN the attempts which have been made to isolate definite organic compounds from soils it has been found that in most cases treatment of the soil with alcohol even at boiling temperature does not give a solution of soil organic matter from which definite results could be obtained.

However, with some soils, characterised usually by a high content of organic matter, this treatment has led to the isolation and identification of definite organic compounds.

The details of the method and the properties of one of the compounds obtained are the subject of this paper.

The soil from which this compound was obtained was the Marshall clay from North Dakota, a black soil containing 10.6 per cent organic matter and 0.51 per cent nitrogen.

When this soil was treated with boiling 95 per cent alcohol there was obtained a greenish brown coloured extract, from which, on cooling, a yellowish microcrystalline precipitate separated. On treating the soil with successive portions of boiling alcohol, the extracts, combined and

* Strictly speaking, we define a perfect solution as one which obeys Equation 4 rather than Equation 5, but the more precise method which employs the activity instead of the vapour pressure leads to exactly the same equation for the osmotic pressure as we shall derive here.

* Presented at the New Haven Meeting, June, 1908, of the American Chemical Society, by permission of the Secretary of Agriculture. From the *Journal of the American Chemical Society*, xxxi., No. 1.

concentrated to smaller volume and allowed to cool, yielded this precipitate in considerable quantity, 250—300 parts per million of soil. This precipitate contained both mineral and organic matter, and is at present the subject of further investigation. The mineral matter is alumina for the most part, and the organic portion is a mixture, some of the so-called waxy acids being present.

The filtrate from this precipitate was a dark greenish brown solution which on evaporation of the alcohol became a thick resinous mass. On treating this residue with cold ether nearly all of the colouring matter went into solution, leaving a small quantity of a yellowish wax-like substance, the nature of which is yet unknown.

The coloured ether solution on evaporation of the ether left again a thick viscous residue. Treatment of this with successive small quantities of cold absolute alcohol removed the colouring matter, leaving a nearly white residue. This residue was readily soluble in ether and crystallised from such solution in needles, usually arranged in radiating clusters. If, however, this body was dissolved in hot 80 per cent alcohol, in which it is quite easily soluble, it crystallised in flat plates very similar in appearance to those of phytosterol.

The compound so obtained melts at 237° (uncorrected), and the melting-point remains unchanged after re-crystallisation. It is readily soluble in ether or chloroform, little soluble in cold alcohol, but readily so in hot, and almost insoluble in hot water. It is unchanged by treatment with alcoholic potash. When crystallised from 80 per cent alcohol it contains water of crystallisation which is lost at 100° .

The appearance and properties of this substance suggested a member of the cholesterol group, and it was found to respond readily to Liebermann's "cholesterol reaction," but gave no reaction with other colour tests for members of this group. Liebermann's reaction is characterised by the violet colour produced when a drop of strong sulphuric acid is added to a solution of the substance in acetic anhydride. This test is best performed by dissolving a very small quantity of the substance in a few drops of chloroform, adding about 1 cc. of acetic anhydride, and then one drop of concentrated sulphuric acid. With the compound from the soil the colour produced by this treatment is intense, appears immediately, and a good reaction is obtained with a very minute quantity. Cholesterol and a number of isomeric substances which have been described are usually represented by the formula $C_{26}H_{44}O + H_2O$. Very little, however, is known of their constitution beyond their alcoholic nature, and even the elementary composition is doubtful, the formula $C_{27}H_{44}O + H_2O$ being given by some investigators.

The composition of the compound obtained from the soil was found to agree very closely with the formula $C_{26}H_{44}O$. The analysis was made with 0.15 grm. dried at 100° . Calculated for $C_{26}H_{44}O$: C, 83.8; H, 11.8. Found: C, 83.6; H, 11.5.

The melting-points of most of the described cholesterol substances are much lower than that of the body obtained from soil. Cholesterol found in animal fats melts at $145-6^{\circ}$, phytosterol found in vegetable fats and waxes melts at $132-3^{\circ}$, isocholesterol found in some animal fats melts at $137-8^{\circ}$, paracholesterol found in etiolated yellow lupines melts at $134-134.5^{\circ}$, sitosterol found in plant fats melts at 137.5° , paraphytosterol found in the seed coat of *Phaseolus vulgaris* melts at 148.50° , parasitosterol found in the embryo of wheat melts at 127.5° , homocholesterol found in Dalmatian insect powder (*Chrysanthemum cinerariaefolium*) melts at 183° , and ergosterol found in ergot melts at 154° . However, anthesterol, a closely related alcohol found in *Anthemis nobilis*, melts at $221-3^{\circ}$ and arnersterol found in *Arnica montana* melts at $249-50^{\circ}$.

The cholesterol substance obtained from the soil does not correspond in melting-point with any substance of this group so far described. For this compound, isolated from a soil, having the chemical properties and general appearance of substances of the cholesterol group, but differing in

melting-point from any of the members of this group so far described, the generic name *agrosterol* is suggested in harmony with the nomenclature of this group.

With regard to the origin of this compound in the soil at least two possibilities present themselves:—It will be seen that several members of the cholesterol group are so far as known found only in single species of plants. It may be that *agrosterol* is characteristic of some plant grown on this soil, and that on the decay of plants of this species it has survived the action of enzymes, fungi, and bacteria, and remained in the soil as an unchanged plant residue. Since, however, the presence of a substance of this group is shown by Liebermann's reaction above mentioned in several soils from widely separated localities with different native vegetation and cropping, it would seem that this suggestion has not much weight. To make this conclusive it would be necessary to show that the substances from different soils giving Liebermann's reaction are really identical, since the reaction is only a class reaction and not specific for *agrosterol* or any other member of the cholesterol group.

On the other hand, it is within the range of possibility that *agrosterol* may be formed from some other substance through the agency of micro-organisms or chemical oxidation. The fact that Lifschütz has shown that a cholesterol substance can be formed by the oxidation of oleic acid emphasises this possibility (*Zeit. Physiol. Chem.*, 1908, lv., 1). The fact that paracholesterol mentioned above is found in slime moulds further supports the suggestion that *agrosterol* may be formed by micro-organisms. *Agrosterol* is very little soluble in water, and saturated solutions of it had no effect on wheat seedlings.

FURTHER INVESTIGATION OF THE ATOMIC WEIGHTS OF NITROGEN AND SILVER.*

By THEODORE WILLIAM RICHARDS, PAUL KÖTHNER,
and ERICH TIEDE.

The Analysis of Ammonium Chloride.

THE subject of atomic weights has acquired new interest recently, because of the striking demonstration by Landolt that the law of the conservation of weight holds true to a great degree of precision in common chemical reactions (Landolt, *Sitzber. Kgl. Preuss. Akad.*, 1908, xv.—xvi., 354). The fact that the sum of the reacting weights remains perfectly constant, within the limit of error of the most exact experimentation, strengthens the conviction that each of these reacting weights possesses fundamental significance. Evidently no error is committed in calculating one atomic weight by subtracting another from the molecular weight of a substance containing two elements, and the whole structure of the table of atomic weights is seen to rest on a satisfactory basis.

These assurances are timely in view of the extraordinary discoveries concerning radio-activity in recent years. Not a few radical thinkers have supposed that these discoveries lessen the importance of exact atomic weight determinations because of the doubt cast on the permanence of the supposed atom, but Landolt's admirable work assures us that under ordinary circumstances the chemical combining proportions are wonderfully permanent, and therefore as full of meaning as they have ever been supposed to be. The new discoveries concerning radio-activity extend the bounds of knowledge, but in no wise lessen the significance of that which went before.

Nitrogen and silver are two of the elements whose atomic weights are at present especially in the focus of attention. Each element is important in many ways because of its frequent occurrence, and each is particularly important in the present connection because of the extent to which the value of its atomic weight is involved with the values of

* *Journal of the American Chemical Society*, xxxi., No. 1.

other atomic weights. Therefore the value of these two should be settled precisely as soon as possible.

During the past one hundred years as many as ninety different investigations, carried out by more than thirty chemists, have been concerned with the atomic weight of nitrogen, and many of these have also had to do with the atomic weight of silver. Most of this work is unsatisfactory in the light of modern knowledge. The compounds of nitrogen and oxygen on the one hand, and silver and oxygen on the other, are not stable enough to be subjected to exact analysis suitable for this purpose; therefore by the chemists both elements have to be evaluated with the help of other compounds, involving other elements. This introduces difficulties upon which many have stumbled.

The physical method of determining molecular weight through gas densities avoids this complication, but, on the other hand, introduces troubles of its own, the chief of which is the difficulty of extrapolating to the ideal condition. It is true that in the case of nitrogen, as Lord Rayleigh has pointed out, the method is especially applicable—but it must of course be supported by chemical evidence to be wholly satisfactory.

Two methods of determining the atomic weight of nitrogen in the chemical fashion have been used by most chemists, namely, the analyses of nitrates and the analyses of ammonium salts. In each of these sets of compounds nitrogen exists in combination with two other elements, but in the case of the nitrates one of these other elements is the standard of the atomic weights itself, namely, oxygen, and in the case of the ammonium salts the two other elements both have many other accurately determined quantitative relations. The study of silver nitrate was undertaken by Stas, and more recently by Richards and Forbes in the chemical laboratory of Harvard College. These results were not very different, and the latter pointed strongly to a value for the atomic weight of nitrogen equal to 14.008, if silver is taken as 107.88; but if silver is taken as 107.93, with Stas, nitrogen will be almost 14.04. It seemed highly desirable therefore to obtain an entirely different set of evidence upon this point through the study of the ammonium halides in their relation to silver—a study which likewise led Stas to a higher value—and the present paper treats the first of a series of investigations upon this subject, concerning the analysis of ammonium chloride.

The history of the analysis of this compound is quickly told. Stas found as an outcome of a number of experiments that 49.597 grms. of ammonium chloride required 100.0000 grms. of silver for precipitation. These analyses, careful as they were, are open to doubt from two causes, one of which has been pointed out by Alexander Scott in an interesting paper upon this subject (*A. Scott, Journ. Chem. Soc.*, 1901, lxx., 147). Scott calls attention to the fact that Stas was never able to prepare ammonium salts wholly free from colour—an evidence that he had never succeeded wholly in eliminating the carbon compounds always present in chemical substances. Scott himself, by means of more drastic treatment, probably succeeded better in this respect.

Unfortunately, both Stas's extensive work and Scott's two analyses of ammonium chloride were evidently inadequate as regards taking account of the solubility of silver chloride, so that these determinations throw but little light upon the question. This deficiency, which occurs in most other early work, is the second cause of doubt concerning Stas's work with chloride.

It is clear, therefore, that the whole subject needs a thorough investigation and revision in the light of modern knowledge concerning both the purity of materials and precision in analysis.

Preparation of Material.—The most important new problem concerning the analysis of the ammonium chloride is the preparation of the material to be used in the analyses, for of course the purity and constant composition of this salt must be beyond suspicion. The impurities most commonly to be found in ammonium salts include various compounds of carbon, and these are usually the most difficult to eliminate. Non-volatile substances, such as salts of the

alkali metals, are of no great consequence. They may easily be eliminated by converting the ammonium salt into ammonia gas and collecting the gas in pure acid.

Stas sought to eliminate the amines by two oxidising processes, one, the treatment of ammonium chloride by nitric acid, and the other, the treatment of ammonium sulphate at high temperature with concentrated sulphuric and nitric acids. Scott used the latter of these methods. These methods undoubtedly decompose most of the amines, but no one has proved that all are eliminated in either of these ways. In view of this doubt it was deemed advisable to use quite another method for the purpose, and nothing seemed more suitable than an application of one of the devices of Kjeldahl for eliminating carbon from ammonium compounds. To every 100 grms. of ammonium sulphate and 75 grms. of concentrated sulphuric acid, contained in a beaker of Jena glass and heated to the point where the sulphuric acid began to volatilise, were added in very small portions a few grms. of finely powdered potassium permanganate. The solution was then heated for many hours to a high temperature until the evolution of carbonic acid and oxygen had ceased and the solution had become wholly colourless—an evidence that the oxidation had reached its limit. After cooling, the cakes of acid ammonium sulphate were dissolved in pure water, and the ammonia was set free by means of freshly prepared milk of lime. The lime for this purpose was made by the ignition of pure calcium carbonate in an electric oven for many hours, and could have introduced no impurity. The simplest method of collecting the gas was found to be the placing of a quartz or platinum dish, containing the purest hydrochloric acid, over the mixture of ammonium sulphate and milk of lime in a vacuum desiccator or ground glass bell-jar. The ammonia quickly transfers itself from the mixture to the acid, and without trouble or danger from spattering the preparation is easily made. This simple method proved itself very much more satisfactory than the attempt to distil the ammonia with steam either from an outside source or by heating the semi-solid mixture of calcium sulphate and ammonium hydroxides. The salt prepared in this way is always beautifully white in appearance. The sample prepared in platinum showed no trace of contamination, but, even supposing a small amount of platinum had been dissolved (see Note), it would have been eliminated by the subsequent sublimation described later. This sample of ammonium chloride is given the designation A in the following pages.

NOTE.—Dr. F. W. Hinrichsen found difficulty from this source, but it is possible that the air was less fully exhausted from his apparatus. In the absence of air the platinum is not attacked (*Zeit. Anorg. Chem.*, 1908, lviii., 59).

No single method of preparation is adequate for a case of this sort, as has often been pointed out. Some entirely different method must be adopted for preparing another sample, in order to be certain that constant impurity has not found its way into the first in spite of all precautions. Stas, realising this, prepared ammonia also by reducing potassium nitrate. He thought that in this way he must obtain a salt free from organic compounds. In the first place he made the nitrite out of saltpetre and lead, and then reduced it by means of zinc and potash. It is by no means certain that these materials were all free from carbon, and if they were not, the doubt concerning the existence of amines synthesised during the process of reduction still remains. Although thus Stas's execution of his idea was not without reproach, the idea was a good one, and we sought to carry it out in another way, using substances really free from carbon, and bringing into play new physico-chemical knowledge. Vortmann (*Ber.*, 1890, xxiii., 2798) made at the beginning of the last decade an observation that under proper experimental conditions it is possible to reduce nitric acid quantitatively to ammonia by means of the galvanic current, provided only that copper is present in the solution and forms the material of the electrodes. In those days the advantage to be obtained

by stirring the solution during electrolysis was not fully realised, but very recently Ingham (*Journ. Am. Chem. Soc.*, 1904, xxvi., 1251) has shown that this process, like all other electrolytic processes, is much hastened in this way. The subject has also been investigated in an empirical fashion by Patten (*Journ. Am. Electrochem. Soc.*, 1907, xii., 325). The experience of this last investigator was not available to us at the time of our work, having not yet been published; accordingly, as the process promised well for the present purpose, Dr. F. W. Hinrichsen (*Zeit. Anorg. Chem.*, 1908, lviii., 59) kindly tested the process with the idea of finding out its efficiency and the best conditions for obtaining high purity of product and maximum yield. This work has already been described in another place. It is enough to say that he found it convenient to use a cathode of copper netting in a cylinder about 10 centimetres in diameter and 10 centimetres high, and an anode of platinum foil, with a current of not over 3 amperes, if the solution was tranquil. It was found advantageous to use a large platinum dish coated inside with copper for the cathode when working with a rotating anode. Equal weights of copper sulphate and re-distilled nitric acid were mixed with about ten times their combined weight of water, and, as the nitric acid was exhausted by reduction and the copper by deposition, more was added. In order to stir the solution he used also the device of Frary (*Zeit. Elektrochem.*, 1907, xiii., 308), by which the solution was whirled by means of the electro-magnetic effect of a surrounding solenoid. Considerable current is needed in order to cause such agitation in the liquid, but the method has the advantage for the present purpose of excluding the danger of dust which comes from any sort of mechanical stirring run by an outside motor. Obviously the pure nitric acid for this purpose, having been twice distilled, was prepared with great care, and diluted with the purest water. The copper sulphate used was also purified by several re-crystallisations. The solution was heated in order to avoid the formation of hydroxylamine, for Tafel has shown that under these circumstances the electrolyte contains less of this substance. (Tafel, *Zeit. Anorg. Chem.*, 1902, xxxi., 282; Patten, *loc. cit.*, apparently never worked above 30°, and accordingly was not able to verify this statement). Even if some had been formed, however, it would have inevitably been decomposed in the later operations. From the ammonium sulphate made in this way pure ammonium chloride was made in the manner already described. This sample was called B.

For a few analyses a cruder preparation was used, made according to Stas's first method by repeated treatment of ammonium chloride with nitric acid, at a boiling temperature, and five re-crystallisations. For freeing the crystals from mother-liquor the new centrifugal apparatus of Richards and Staehler was employed. A fourth preparation, prepared by a student at Harvard by the same process, was also used for two analyses. These two similar preparations, possibly less pure than the others because of the method used in their preparation, were called C and D.

The ammonium chloride thus prepared was—at least, as regards samples A and B—very pure with the exception of the presence of an excess of hydrochloric acid and water. Most of the preparations showed a feebly acid reaction after evaporation to dryness. They were each re-crystallised several times out of water containing a little ammonia prepared by the same process. These crystallisations were effected in quartz or platinum dishes, and the heating was conducted by electricity in order to avoid contamination from illuminating gas. Needless to say, dust was excluded as carefully as possible. The mother-liquor was separated as usual by means of the platinum centrifuge of great power. The preparation thus obtained was snow-white and possessed a slight smell of ammonia. It was dried in a vacuum desiccator and kept over potash in quartz or platinum dishes. The final preparation of this material for analysis was by sublimation. Each sample was sublimed twice immediately before analysis, collecting

it the second time in the vessel in which it was to be weighed. This operation will be discussed in a subsequent chapter.

All the other substances, water, hydrochloric, nitric, and sulphuric acids, silver, calcium carbonate, &c., were prepared by essentially the methods which have been used for a number of years in Harvard University and are described in detail in the various papers from that institution, especially in *Publication 69* of the Carnegie Institution of Washington. There is no need of reviewing these well-known methods. It goes without saying that great care was taken to avoid the use of utensils whose solubility could contaminate the products or influence the reactions. Whenever possible quartz dishes were used with acid liquids, and platinum ones with alkalis; and where glass was unavoidable the best Jena glass was employed. Electric heating was used almost universally in order to avoid objectionable products of combustion. For vacuum work the convenient, almost automatic mercury pump of Ubbelohde-Stock was used with profit, and apparatus was constructed without rubber connections, being fused together wherever it was possible. For the necessary glass joints a paraffin lubricant of vanishingly small vapour tension was kindly given us by Professor Brauner, of Prague. Many bell-jars served to protect the substances from dust and objectionable gases. The laboratory was a room in the First Chemical Institution of Berlin especially dedicated to the purpose through the kindness of Geheimrat Emil Fischer, and this room was kept as free as possible from soluble gases of all kinds. The quantitative work was carried out in an especial room used by the experimenter alone, and another special room served for the balance. The dark-room used for the preparations was not interfered with by any other investigation during the time while this was in progress.

All these favourable conditions contributed greatly to the success of the undertaking. Without advantages of this sort much time and experimental energy may be wasted, because one's efforts are rendered vain by the inevitable introduction of impurities from the atmosphere. Not only in this way, but also by providing plentiful apparatus of rare and expensive kinds, Professor Fischer did much to further the work, and we take great pleasure in recording our grateful thanks. To Dr. A. Staehler we are also greatly indebted for his kindness in attending to the arrangement of the laboratory, and for help in many details.

(To be continued).

Optical Investigation of the Copper Complexes in Ammonia and Pyridine Solution.—A. Hantzsch and P. W. Robertson.—All cupric compounds are optically identical in all aqueous and alcoholic ammonia solutions, and contain only the complex $\text{Cu}(\text{NH}_3)_4$ as chromophor. All copper solutions with the complex $\text{Cu}(\text{NH}_3)_4$ are unaffected by changes of temperature, solvent, &c. Apparent alterations are to be ascribed to changes in the complex, e.g., to the formation of the complex $\text{Cu}(\text{NH}_3)_3$. All copper salts are optically identical in aqueous pyridine; the copper pyridine complex is less stable than copper tetrammine, and has the composition CuPy_3 . Copper acetate solutions contain another complex of formula $\text{Cu}(\text{Py}_2(\text{OAc})_2)$ in pure and alcoholic pyridine solution. Copper acetate solutions in water, methyl, ethyl, and amyl alcohol are optically different, and contain different complexes. From the fact that water and alcohol on entering the complex alter its colour, it follows that copper tetrammine is dissolved in all solutions as such and not in the form of a complicated complex of formula $\text{Cu}(\text{NH}_3)_4$, for instance. Thus copper only forms complexes of the type CuR_4 , and its co-ordination number is 4.—*Berichte*, xli., No. 17.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY OF NEW SOUTH WALES.

General Monthly Meeting, December 2nd, 1908.

W. M. HAMLETT, F.I.C., F.C.S., President, in the Chair.

The following papers were read:—

"The Discontinuity of Potential at the Surface of Glowing Carbon." By J. A. POLLOCK, A. B. B. RANCLAUD, and E. P. NORMAN.

In a circuit with one heated electrode in air at ordinary pressure, the projection of ions from the hot surface necessitates the establishment of a potential difference between the electrodes if the current in the circuit is to be zero. This potential difference under certain circumstances may be taken as a measure of the surface discontinuity, and values have been obtained in the case of glowing carbon at various temperatures.

Abstract of lecture on *"John Dalton and One Hundred Years of the Atomic Theory."* (Illustrated by diagrams and models). By F. B. GUTHRIE, F.I.C., F.C.S. Delivered November 19th, 1908.

The lecturer after shortly reviewing Dalton's life discussed the position of the Atomic Theory in the development of the science. The history of chemistry since Dalton has been the development, extension, and modification of the theory. Previous conceptions of the atomic structure of the Greek were then discussed, notably those which we owe to the Greeks and Lucretius, and it was shown that, though it is customary to regard Dalton's theory as a development of the Greek, Dalton's conception of the atoms differed fundamentally from theirs. As first enunciated the law explained satisfactorily certain phenomena then for the first time noticed, but was not free from objection owing to confusion arising between the conceptions of atoms and of compound atoms or molecules, and owing also to an arbitrary assumption on Dalton's part as to the proportions in which the elements combine, as well as to the difficulty in correctly determining the atomic weights. These difficulties were got over largely by the acceptance of the important law known as Avogadro's law, and the discovery of relationships between the atomic weights and the physical properties of the elements which enabled the atomic weights to be verified with considerable accuracy. It was soon found that a very profound and highly significant relationship existed between the atomic weights of the elements and their general properties. This was first observed by Newlands the English chemist, but developed later by Mendeleeff into the Periodic Law. This highly important generalisation, based as it is on the atomic theory, is one of the most important achievements of this theory. In other directions the atomic theory has developed in ways equally important and unforeseen. By its means chemists have been able to learn something of the constitution of the most complex forms of matter. The doctrine of valency introduced by Frankland is a direct corollary of the atomic theory. The modern development of the theory of valency has led us to the most ingenious and beautiful explanations of the internal groupings of the atoms in chemical substances, and has been especially prolific in the discovery and synthesis of new substances in the benzene group, notably the dyes and other remarkable substances known as the coal-tar derivatives. It has also served to explain the remarkable optical behaviour of substances otherwise identical. At the present time we are undergoing a change in our conception of the nature of the atom. Research into the electrolysis of solutions, the ionisation of gases, and radio-activity have familiarised us with the idea that the atom is not to be regarded as indivisible, but as composed of yet smaller particles—electrons—the escape of which from the atom give rise to the phenomena of radio-activity. All these manifestations

can only be satisfactorily explained on the assumption that what we observe is the disintegration of the atom, and that the energy is derived from the internal energy, a view which brings us to the new conception that the atomic weight is a function of the internal energy of the atom. We are also familiarising ourselves with the idea that it is quite possible that the elements are mutually convertible. We have become familiar with the notion that the so-called radium emanation passes over into helium, and in recent papers by Ramsay and Cameron, these authors consider that the effect of the action of emanation upon water and copper sulphate is to produce the gases neon and perhaps argon, whilst in the case of the action on copper sulphate the copper would appear to be degraded into lithium and sodium. In the case of the formation of neon the authors consider it to be indisputably proved. In the other cases they are less certain. These modifications must not be regarded as upsetting or supplanting the atomic theory, but merely as rendering necessary some modification of our present conceptions of the atom; notably its invariability and indivisibility.

NOTICES OF BOOKS.

Sketches from the Life of Sir Edward Frankland, K.C.B.

Edited and Concluded by his two Daughters M. N. W. and S. J. C. London: Spottiswoode and Co., Ltd.

THE student of physical science often feels the want of some general reading in the subjects which specially interest him, quite apart from his academical work and yet in some way bearing upon it. This want cannot be better supplied than by biographical literature, and the peculiar charm of a good autobiography is very marked in this book. The story of Sir Edward Frankland's life is told almost entirely in his own words; the awakening of his interest in experimental science and his subsequent devotion to the subject are described in vivid language, and chapters on the researches which he brought to a successful conclusion, and by which he gained so much renown, give a summary of his activity in the scientific world. These chapters are excellent reading for students of organic chemistry, who will always find it worth while to make themselves acquainted with the original papers of investigators, especially when their work is that of a genuine pioneer. Special attention must be called to the discussion of Frankland's work on the determining factors of the luminosity of flames, which is far too little known. Delightful chapters on the author's experiences on his travels show him to have been, as indeed his whole career pointed out, a man of keen appreciations, lively interests, and wide culture. Though parts of the autobiography may be too technical for the general public, many portions of it will interest every reader, who will gain from it an acquaintance with the charming personality of a man of genius, whose letters show quick powers of observation and deep insight.

Recent Advances in Organic Chemistry. By A. W.

STEWART, D.Sc. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1908.

THIS book can only be described as simply invaluable for students of organic chemistry. To many the study of organic chemistry means nothing more than the acquirement by rote of a greater or smaller number of facts, the meanings and correlation of which are practically passed over altogether, and the extinction of this wholly false view is one of the aims of the author, while the constructive object is to stimulate the reader's own critical and selective powers to follow the most modern advances in methods of thought and argument. Exceedingly clear accounts are given of methods of synthesising newly discovered com-

pounds among the polyketides, polymethylenes, polypeptides, alkaloids, &c., and for these alone the book has a special value as providing a key to the bewildering accumulation of details which is to be found in articles appearing in periodicals dealing with organic chemistry. But the book is more than an account of the work which has already been done; it points out the methods by which the almost countless facts which have been ascertained by research will be brought into relation with one another, and how order will be made out of them. Although the connection between physical properties and chemical constitution is only lightly touched upon, the author's belief that we are standing on the brink of a revolution in our views upon the fundamental questions of organic chemistry is discussed in an interesting concluding chapter. An introduction calling attention to the special features of the work has been written by Prof. Collie.

Chapters on Papermaking. Vol. V. By CLAYTON BEADLE. London: Crosby Lockwood and Sons. 1908.

THE fifth volume of this text-book of paper making deals with the theory and practice of beating, and is mainly occupied with the description of tests carried out by the author with different types of machines and different classes of materials. The book thus provides a good deal of numerical information upon which a thorough scientific knowledge of the subject of beating may be based; much of it has not been published before. Every effort has been made to obtain reliable and comparable data, and the tests carried out relate to the maximum power consumption of different types of machines, the relative merits of stone and metal beater bars, power consumed in grinding wood pulp in comparison with that required for beating, &c. A conspicuous merit of the book is the clearness with which it treats in a popular style of a branch of paper-making which has hitherto been somewhat neglected, and thus it lays the foundation for a fuller and more comprehensive study of the theory and practice of beating.

Leather, Technical and Practical. London: The Leather Trades Publishing Company.

THIS new monthly journal for all engaged in the leather industries will undoubtedly meet a want, and if the first number may be accepted as an average specimen of what it will provide, it will very soon make a place for itself in the scientific and technical world. The journal opens with an article upon "Some Unsolved Problems in Leather Chemistry," by Prof. Procter, in which an interesting account is given of the directions in which our knowledge of the chemistry of leather manufacture will probably develop in the immediate future. Other original articles, which are to be a conspicuous feature of the new paper, include one on "The Quality of Sole Leather" and on "Chrome Liquors and their Application," which, though short, contain the essential points of the subjects they deal with. Sets of model answers to the City and Guilds of London Institute's Examinations in Leather Dyeing, Staining, and Finishing will be useful both to students who are preparing for the examinations, and to practical men whose knowledge of certain aspects and details wants rubbing up or extending. Short abstracts from foreign journals and reviews of recently published books fill up the paper, for the success of which we may express cordial and confident hopes.

Organic Chemistry. By A. E. DUNSTAN, B.Sc. London: Methuen and Co.

THIS text-book of organic chemistry does not follow the syllabus of any particular examination, but gives a course designed for the higher classes in science and other schools and for the first year students in technical colleges. Suitable practical work is included, both preparations and methods of identifying an organic compound being de-

scribed. The book begins with a study of the preparation and properties of alcohol and its reactions. Then its oxidation and reduction products are described, as well as the principal characteristics of its homologues. These subjects occupy the first ten chapters. Then acetic acid is made the starting point of a fresh group of compounds—acid chlorides, nitriles, amides, &c.—and various typical reactions are explained. This centralising of all the beginner's knowledge round one compound is an excellent plan, tending to consolidate his ideas, and slight though the treatment of some reactions is, it is sufficient to give the student an idea of the main general reactions of organic chemistry. The later chapters of the book introduce many new classes of compounds, unsaturated dibasic acids, glycerols, carbohydrates, &c., and, in fact, this part is a little congested. However, this drawback could probably be met by spreading the course over a longer period than a year, and allowing the student to supplement the book by the use of a larger treatise containing in particular more purely theoretical matter.

Producer-Gas and Gas-Firing. By ERNEST SCHMATOLLA. London: Published by the Author. 1908.

THIS booklet, which is an abridgment of the second edition of "Gas Producers and Gas-Firing," gives a summary of the advantages to be gained by the use of producer-gas instead of coal in works employing furnaces. In it are described methods of making the gas and mixing it with air, and the results obtained with cheap fuels used in producers are compared with those given by high-class fuels used in the ordinary way; without going into details or giving statistics the author makes it clear how great saving can be effected, while the efficiency of the furnace is by no means impaired. Undoubtedly it is in the extended use of producer-gas that the solution of the smoke problem will in some degree be found, and such pamphlets as this are of great value in calling the attention of practical men to improvements and economies which have been subjected to tests and have been found to be feasible.

The Chemistry of Essential Oils and Artificial Perfumes. By ERNEST J. PARRY, B.Sc. (Lond.), F.I.C., F.C.S. Second Edition. London: Scott, Greenwood, and Son. 1908.

THE chemistry and technology of the essential oils are fully treated in this book, which has been considerably enlarged in preparing the second edition. The compounds contained in essential oils are first described, and the usual methods of preparing the oils are explained and illustrated. The analysis of the finished product is dealt with in outline only, no attempt being made to provide a laboratory guide for analytical work. The greater part of the book is occupied with the systematic study of the chemical and physical characteristics of the oils; these are grouped according to the botanical relationships of the plants yielding them, which is, on the whole, the most satisfactory method of classification. An outline is given of the chemistry of artificial perfumes, and to the second edition an appendix has been added, showing in tabular form the requirements of the British and ten of the most important foreign Pharmacopœias.

Annuaire pour l'An 1909 publié par le Bureau des Longitudes. ("Annual for the Year 1909 Published by the Longitude Bureau"). Paris: Gauthier-Villars.

IN accordance with the usual custom of alternating certain kinds of information each year this, the 113th volume of the *Annuaire* issued by the Bureau des Longitudes, contains data relating to meteorology and geography and general statistics, in addition to the usual copious astronomical tables. The annual for 1910 will contain lists of physical and chemical constants. The astronomical tables are marvels of completeness, and in addition the annual

contains two articles, one by G. Bigourdan on the variable stars, and the other by Ch. Lallemant on the movements and deformations of the crust of the earth.

CORRESPONDENCE.

THERMO-CHEMICAL POTENTIAL AS A MEASURE OF CHEMICAL AFFINITY.

To the Editor of the Chemical News.

SIR,—The considerations which have led me to consider the elements as possessing thermo-chemical equivalents which are approximately correct when tested against the large mass of thermo-chemical data, also point direct to these equivalents being perhaps the readiest measure of chemical affinity.

I select the four most common non-metallic elements, carbon, hydrogen, nitrogen, and oxygen, and quote the equivalents I have endeavoured to establish for these in previous numbers of the CHEMICAL NEWS (vol. xciii., *et seq.*).

The high value given for oxygen at once shows the reason for water and carbon dioxide being the most stable of the ordinary compounds of these elements.

Methane, ethane, and carbon monoxide, with heats of formation of a similar value, are approximately equally stable, ammonia (NH₃) lying between these compounds and the nitrogen oxides in which I represent oxygen as penta-valent, and which are unstable compounds, nitrous oxide (N₂O) being least so.

In using the term thermo-chemical potential, I think it adequately supplies a connecting link between what at first I merely regarded as a heat exchange between the elements, and now consider as also a measure of affinity. —I am, &c.,

J. C. THOMLINSON, B.Sc.

January 19th, 1909.

POTENTIAL ENERGY OF THE ELEMENTS.

To the Editor of the Chemical News.

SIR,—With reference to Mr. J. C. Thomlinson's letter (CHEMICAL NEWS, xcix., 34) in which he seeks to establish a relationship between the potential energy of the elements and their atomic weights, I venture to offer the following observations:—

The atomic weights may be defined as the weights of masses which under similar conditions are similar functionals of their absolute atomic potentials. A chemical combination is essentially the result of an interaction of potential energy, and the ratios of the weights of the elements taking part are simply functionals of the absolute values of potential concerned in such reaction.

May I observe further that, in my view, Dalton's conception of the atom as a sphere surrounded by a zone or atmosphere of free energy has not received the attention it merits.

We may conceive the zone to be composed of imponderable (in the sense that it cannot be detected by the aid of a chemical balance) potential or unequilibrated energy, and to envelope a central nucleus of ponderable equilibrated or static energy.

A ratio between these two fundamental states of energy admits of calculation, and affords an important factor in the estimation of the value of the potential energy of the element. This conception also furnishes data for an entirely different and more concrete view of the nature of chemical change than that now in vogue, but which I would prefer not to enlarge upon at present.—I am, &c.,

DANIEL J. RANKIN.

Orleans House, Peterborough,
January 18th, 1909.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xli., No. 17, 1908.

Synthesis of Alcohols of the Series C_nH_{2n-5}.OH—A. Reformatsky.—The action of allyl iodide and zinc on the esters of the halogen substituted acids in ethereal solution may be regarded as a general method of preparing monatomic unsaturated alcohols of the series C_nH_{2n-5}.OH. Glycols or oxyacids or their lactones are also formed. The yields of alcohols and the corresponding condensation products are in inverse proportion; also the higher the molecular weight of the ester the smaller the amount of alcohol formed and the greater the amount of the condensation product. The intensity of the reaction decreases as the molecular weight of the halogen substituted ester increases, and substituted esters of abnormal structure give poorer yields of alcohol and larger quantities of condensation product. The esters of brom-substituted acids react more energetically than those of chlor-substituted acids. All the alcohols of the series prepared by the author are colourless liquids smelling like the terpenes; they are insoluble in water, and readily soluble in alcohol and ether. They are not appreciably oxidised in the air, but are readily brominated and oxidised by potassium permanganate.

New Method of Formation of Liquid Alloys of Sodium and Potassium.—George F. Jaubert.—When potassium acts on caustic soda and when sodium acts on caustic potash, alloys of sodium and potassium are formed; they may contain up to 80 per cent of potassium. The chief reaction between K and NaOH may be expressed by the equation $3K + NaOH = KOH + NaK_2$, while between Na and KOH it is $3Na + 2KOH = 2NaOH + NaK_2$, or, if less heat is applied, $2Na + KOH = NaOH + NaK$. Both the alloys NaK and NaK₂ are liquid.

Chlorazide, N₃Cl.—F. Raschig.—When a solution of the sodium salt of hydrazoic acid, N₃Na, is mixed with a solution of sodium hypochlorite and the mixture is acidified with a weak acid, such as acetic or boric acid, it turns yellow, and a colourless gas escapes, smelling of hypochlorous acid. The gas explodes when brought into contact with a flame or a glowing splinter. It is soluble in water, giving a yellow solution. The gas escapes from this solution at the ordinary temperature *in vacuo*, and can be collected in caustic soda; the solution thus obtained sets iodine free from potassium iodide, and bleaches litmus-paper. The composition of the gas is expressed by the formula N₃Cl, and the equation showing its formation is $HOCl + N_3H = H_2O + N_3Cl$, the action being similar to that of hypochlorite on ammonia, $HOCl + NH_3 = H_2O + NH_2Cl$. When the solution of chlorazide acts on caustic soda sodium hydrazide and sodium hypochlorite are formed.

Chromium Compounds.—A. Werner and N. Costachescu.—Two fluorides of the hexaquo chromium series exist, the normal [Cr(OH₂)₆]F₃ and the esotrihydrate [Cr(OH₂)₆](OH₂F)₃. They are both violet in colour. Two hexafluorochromates of the hexaquo series are known, namely, the normal [Cr(OH₂)₆](CrF₆) and the monoesohydrate [Cr(OH₂)₆](CrF₆)·H₂O. An isomer of the latter is trifluorochromium, which can be represented by the constitutional formula $2 \left[Cr \begin{smallmatrix} (OH_2)_3 \\ F_3 \end{smallmatrix} \right] + 1H_2O$.

The three last chromium fluoride hydrates are given.

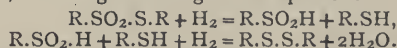
Action of Phosphorus Pentachloride and Pentabromide on Mercaptans.—W. Autenrieth and Alfred Geyer.—Pure phenyl and benzyl mercaptans react very violently at the ordinary temperature with both PCl₅ and PBr₅. When the mercaptan is cooled an energetic reaction also occurs, hydrochloric acid being evolved.

From quantitative experiments it has been found that the course of the reaction is expressed by the equation $2\text{C}_6\text{H}_5\text{SH} + \text{PCl}_5 = \text{C}_6\text{H}_5\text{S}.\text{SC}_6\text{H}_5 + \text{PCl}_3 + 2\text{HCl}$. Thus the products are PCl_3 or PBr_3 , disulphide and hydrogen haloid. No by-products can be detected.

Constitution of Disulphoxides.—O. Hinsberg.—The synthesis of ethyl disulphoxide by potassium ethylthiosulphonate and ethyl bromide,—



seems to point to the fact that the disulphoxide has the asymmetrical formula, but the author points out that the alkyl thiosulphonates have undoubtedly the formula $\text{R}.\dot{\text{S}}(\text{O}).\text{S}(\text{O}).\text{R}$ and not $\text{RSO}.\text{S}.\text{OMe}$ as Gutmann assumed. When disulphoxides are reduced, disulphides are formed, $\text{C}_{10}\text{H}_7.\text{SO}.\text{SO}.\text{C}_{10}\text{H}_7 + 4\text{H} = \text{C}_{10}\text{H}_7.\text{S}.\text{S}.\text{C}_{10}\text{H}_7 + 2\text{H}_2\text{O}$, but although this seems to point to the symmetrical formula there is always the possibility that the reaction is complicated, occurring according to the equations—



This assumption, however, appears to be contradicted by the regular course of the reduction process, while no sulphinic acid nor mercaptan can be detected. The author considers that the symmetrical formula of the disulphoxides is by far the most probable.

MISCELLANEOUS.

Institute of Chemistry.—Pass List, January Examinations, 1909.—Of nineteen candidates who presented themselves for the Intermediate Examination, the following eleven passed:—M. S. Baker; R. Boyd, B.Sc. (Glas.); W. G. Carey; H. S. Coupland, B.Sc. (Lond.); S. E. Crook; H. R. Lyell; A. Marcan; G. S. McKee; F. J. L. Petri; J. Shelton; and N. Garrett Smith. Eight candidates presented themselves for the Final Associateship Examination in the Branch of Mineral Chemistry, and three passed:—T. W. Harrison, B.Sc. (Lond.); J. R. Hill, B.A. (Cantab.); and N. M. Hyslop. In the Branch of Metallurgical Chemistry, of two examined, one passed:—Charles Salter, Assoc.R.C.Sc., A.R.S.M. Of eight candidates who presented themselves in the Branch of Organic Chemistry, the following six passed:—H. T. Clarke, B.Sc. (Lond.); H. Davies; J. G. Hay; V. J. Harding, B.Sc. (Manc.); G. Hogan; and J. H. Ryffel, M.A. (Cantab.), B.Sc. (Lond.). In the Examination in the Chemistry of Food and Drugs, and of Water, of nine who presented themselves, four passed:—W. Bacon, B.Sc. (Lond.); B. S. Evans, B.Sc. (Lond.); O. J. Patrick; and V. J. Tilley. W. Bacon and J. H. Ryffel were examined for the Fellowship.

Royal Institution.—On Tuesday next, February 2, at three o'clock, Prof. A. A. Macdonell begins a course of three Lectures at the Royal Institution on "The Architectural and Sculptural Antiquities of India." During the course the Buddhist, Hindu, and Muhammadan antiquities will be dealt with, and illustrated with lantern slides. Mr. William Archer is to give two Lectures, commencing February 11, on "The Revival of Modern Drama," in which its causes and problems will be discussed. On Saturday, February 6, Sir Alexander Mackenzie commences a course of three musical lectures, the first two of which will be devoted to Mendelssohn, and the remaining one to Chamber Music. The lectures will be musically illustrated with the kind assistance of the Hans Wessely Quartette. The Friday Evening Discourse on February 5 will be delivered by Prof. J. G. Frazer on "The Influence of Superstition on the Growth of Institutions," and on February 12 by Prof. H. A. Wilson on "The Electrical Properties of Flame." The Discourse on February 26 will be delivered by Prof. H. L. Callendar on "Osmotic Phenomena" instead of by the Earl of Berkeley.

Essay Competition on Radium.—Young scientists connected by birth or residence with the county of Dorset will be interested in the essay-writing competition announced in our advertising columns to-day. The "Cecil" Medal and Prize will be awarded for the best Paper on "The Discovery of Radium; Its Probable Origin, Present Development, and Possible Future Use." The competition will be open to any person who was between the ages of eighteen and thirty on May 12th, 1908 (that being the date of the Annual Meeting of the Dorset Field Club, under whose auspices the competition is held), and who was either born in Dorset or had on May 12th, 1908, resided in the county for the previous twelve months. Papers for both medals must be clearly written, and may be illustrated by drawings or photographs, the personal work of the candidate. The committee attach great importance to original observation. Papers should be sent by March 1st, 1909, to Nelson M. Richardson, Esq., Montevideo, near Weymouth. Further particulars may be obtained of the Assistant Secretary, Mr. H. POUNCY, Chronicle Office, Dorchester.

NOTES AND QUERIES.

*. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Coal-tar Acids.—Can any reader recommend a good book containing account of the separation and estimation of the various tar acids, &c., of coal-tar?—PHENOL.

MEETINGS FOR THE WEEK.

- MONDAY, Feb. 1st.**—Royal Institution, 5. General Monthly Meeting. Royal Society of Arts, 8. (Cantor Lecture). "Public Supply of Electric Power in the United Kingdom," by G. L. Addenbrooke.
- Society of Chemical Industry, 8. "Gun-cotton and its Manufacture," by Col. Sir Frederick L. Nathan, R.A.
- TUESDAY, 2nd.**—Royal Institution, 3. "Architectural and Sculptural Antiquities of India," by Prof. A. A. Macdonell.
- Royal Society of Arts, 4.30. "Production of Wheat in the British Empire," by Albert E. Humphries.
- WEDNESDAY, 3rd.**—Society of Public Analysts, 8. (Annual General Meeting). "Use of Quartz Combustion Tubes, especially for the Direct Determination of Carbon in Steel," by B. Blount and A. G. Levy. "Composition and Analysis of Chocolate," by P. A. E. Richards, C. H. Cribb, and N. P. Booth. "Some Commercial Samples of Monobrombenzene," by J. H. Coste.
- Royal Society of Arts, 8. "The Problem of Unemployment," by Bolton Smart.
- THURSDAY, 4th.**—Royal Institution, 3. "Revival of Modern Drama," by William Archer, M.A.
- Chemical, 8.30. "The Triazo-group—Part VII., Interaction of Benzhydoximic Chloride and Sodium Azide," by M. O. Forster. "The Triazo-group—Part VIII., Azoimides of the Monobasic Aliphatic Acids," by M. O. Forster and R. Müller. "Nitro-derivatives of Ortho-xylene," by A. W. Crossley and Miss Nora Renouf. "Divergence of the Atomic Weights of the Lighter Elements from Whole Numbers," by A. C. G. Egerton. "Benzyl and Ethyl Derivatives of Silicon Tetrachloride," by G. Martin and F. S. Kipping. "Constituents of the Bark of *Prunus serotina*—Isolation of l-Mandelonitrile Glucoside," by F. B. Power and C. W. Moore. "Mechanism of the Reduction of Nitro-anilines and Nitro-phenols" and "Relation between the Strength of Acids and Bases and the Quantitative Distribution of Affinity in the Molecule," by B. Flürscheim. "Simple Notation for Indicating the Configuration of the Sugars and Allied Substances," by T. S. Patterton. "Determination of the Rate of Chemical Change by Measurement of the Gases evolved," by F. E. E. Lamplough. "Formation and Reactions of Imino-compounds—Part VIII., The Formation of Methyl Derivatives of 1,3-Diamino-2-phenyl-naphthalene from the three Tollylacetoneitriles," by S. R. Best and J. F. Thorpe. "Effect of Conjugated Unsaturated Groups on Optical Activity," by T. P. Hilditch.
- FRIDAY, 5th.**—Royal Institution, 9. "Influence of Superstition on the Growth of Institutions," by Prof. J. G. Frazer, D.C.L.
- SATURDAY, 6th.**—Royal Institution, 3. "Mendelssohn" (with Musical Illustrations), by Sir Alexander C. Mackenzie.

TABLE II.

Volume in cc. of HCl containing 293.9 grms. per litre	50	50	0
Volume of solution when titration was started	1000	1000	1000
Volume of MgSO_4 solution containing 246 grms. crystallised salt per litre	200	100	100
True value	13'45	13'45	13'45
20 cc. Fe'' solution	14'52	14'79	13'55
First addition of 20 cc.	13'69	13'36	13'40
Second addition of 20 cc.	13'35	13'46	13'40
Third addition of 20 cc.	13'08	13'29	13'40
Fourth addition of 20 cc.	13'48	13'43	—
Fifth addition of 20 cc.	13'41	13'36	—

TABLE III.

Volume in cc. of HCl containing 293.9 grms. per litre	50	50	0
Volume of solution when titration was started	1000	1000	1000
Volume of Na_2SO_4 containing 142 grms. anhydrous salt per litre	200	100	100
True value	12'21	12'21	12'21
20 cc. Fe'' solution	13'39	13'56	12'42
First addition of 20 cc.	12'35	12'69	12'20
Second addition of 20 cc.	11'95	11'57	12'12
Third addition of 20 cc.	12'03	11'95	12'19
Fourth addition of 20 cc.	12'13	12'03	—
Fifth addition of 20 cc.	12'02	11'93	—

TABLE IV.

Volume in cc. of HCl containing 293.9 grms. per litre	50	50	0
Volume of solution when titration was started	1000	1000	1000
Volume of $(\text{NH}_4)_2\text{SO}_4$ solution containing 132 grms. $(\text{NH}_4)_2\text{SO}_4$ per litre	200	100	100
True value	13'45	13'45	13'45
20 cc. Fe'' solution	14'95	14'89	13'62
First addition of 20 cc.	14'23	14'65	13'34
Second addition of 20 cc.	13'86	13'88	13'34
Third addition of 20 cc.	13'86	13'86	—
Fourth addition of 20 cc.	13'81	13'77	—
Fifth addition of 20 cc.	13'78	13'73	—

carried out in which the amounts of hydrochloric acid and the dilution were varied.

The numbers obtained are tabulated in Table I. The approximately decinormal permanganate solution was titrated with the ferrous solution in presence of sulphuric acid alone every day before work was begun, the numbers obtained appearing in the "true value" row of Table I.

It will be seen from the table that the mean of rows I. and II. is always too large, and that of rows II. and III. and of all the succeeding titrations taken in pairs is, in general, too small.

Further, there appears to be no special advantage in taking means at all, the second titration of every series being as good an approximation to the "true value" as the mean of the second and third or third and fourth.

The numbers, as will be seen from the rows containing the differences, are not in close enough agreement with the true value to warrant the process being used to give any but very approximate results.

It is also apparent that very small amounts of hydrochloric acid have considerable effect on the titration, and also that the influence of dilution is very small.

The results are, if anything, slightly better in concentrated than in dilute solution; a fact opposed to the general idea that titration in presence of hydrochloric acid should only be carried out after diluting largely. The subject is complicated by the difficulty of obtaining a sharp end-point.

After the titration has been started the solution turns yellowish green, and a chlorinaceous smell is noticed.

The colour change on completion of the titration is to a reddish brown instead of to the usual clear pink tinge.

As might be expected, the change becomes less and less easy to see as the amount of manganous and ferric salt increases. Increase of concentration has the same effect, and in the column left blank in Table I. there was no visible end-point.

II. Titration in presence of Various Salts.

(a) *Magnesium Sulphate*.—Table II. shows the results obtained when a strong solution of magnesium sulphate was added before titration. It appears to have no effect at all. Throughout the titrations a strong chlorinaceous smell was noticed.

(b) *Sodium Sulphate* (Table III.).—This salt is also without effect.

(c) *Ammonium Sulphate* (Table IV.).—In this case the results are not only no better, but actually worse. The gas evolved had quite another smell than chlorine, and was reminiscent of chlorine monoxide. It is not surprising that the results in this case should all be too large, since chlorine acts with considerable ease on ammonium salts,

TABLE V.

Volume in cc. of HCl containing 293.9 grms. per litre	50	50	50	50	50	50	50	50
Volume of solution when titration was started	1000	1000	1000	1000	1000	1000	1000	1000
Volume of MnSO_4 solution containing 150 grms. crystallised salt per litre	200	150	100	50	25	25	10	0
True value	13'47	13'47	13'47	13'47	13'47	13'47	13'47	13'47
20 cc. Fe'' solution	13'66	13'66	13'61	13'73	13'87	13'82	13'74	14'43
First addition of 20 cc.	13'40	13'48	13'52	13'49	13'52	13'46	13'03	13'64
Second addition of 20 cc.	13'43	13'47	13'45	13'40	13'29	13'43	13'50	13'51
Third addition of 20 cc.	13'46	13'35	13'45	13'48	13'40	13'39	13'32	13'26
Fourth addition of 20 cc.	13'24	13'44	13'45	13'37	13'33	13'31	13'47	13'45
Fifth addition of 20 cc.	13'46	13'32	13'36	13'39	13'44	13'48	13'27	13'45

Mean of—

I. and II.
II. and III.
III. and IV.

Difference of mean of II. and III. from true value.. .. .

—0'06 0'00 +0'01 —0'03 —0'07 —0'03 —0'21 +0'10

giving nitrogen trichloride to which the pungent smell may have been partly due.

(d) *Manganese Sulphate* (Table V.).—There is no doubt that if particular care is taken to standardise the permanganate under approximately the same conditions as will obtain when the unknown ferrous solution is titrated, the strength of an iron solution can be obtained even in presence of hydrochloric acid, if a considerable excess of manganous sulphate is first added (Hauffe, *Chem. Zeit.*, 1897, xxi., 894; Willenz, *Chem. Centr.*, 1899, i., 638). In order to ascertain if numbers could be obtained which would agree with the titre of a ferrous solution found in the ordinary way, in presence of sulphuric acid alone, a series of titrations was carried out in which a varying amount of manganous sulphate was added to the mixture before titration. Twenty cc. of the ferrous solution were mixed with 50 cc. HCl and 25 cc. of dilute H_2SO_4 , the $MnSO_4$ added, and the volume of the solution brought up to 1 litre with distilled water.

Table V. contains the numbers found. It will be seen that the mean of II. and III. agrees well with the true value, provided there is a fair amount of manganese salt present.

This method of working, therefore, gives fairly good results, but it is cumbersome, owing to the large amount of solution to be dealt with, and also inconvenient owing to the necessity for having enough iron solution to serve for three titrations.

The colour change, as was the case in the first series of titrations, is peculiar, a brown tint being taken to mark the disappearance of the last trace of ferrous salt.

The end-point is at first well marked, but becomes more and more indefinite as the amount of ferric salt increases.

In one case in which the solution was only diluted to 250 cc. there was no visible end-point, the solution gradually darkening to brown.

In general, no smell of chlorine was noted, but in the two cases in which 25 cc. of manganous solution were added, there was a very slight one, and in the case with 10 cc. the smell was very distinct.

It seems probable that the manganous salt keeps the chlorine from escaping from the solution with the consequent formation of a brown compound, rather than that it prevents the reaction between the hydrochloric acid and the permanganate from taking place.

(To be continued).

THE OSMOTIC PRESSURE OF CONCENTRATED SOLUTIONS, AND THE LAWS OF THE PERFECT SOLUTION.*

By GILBERT NEWTON LEWIS.

(Continued from p. 53).

IN Table IV. the osmotic pressures of cane-sugar solutions are calculated from Equation 7. The first column gives the weight normal concentration; the second, the volume normal; the third, N_1 , the mol. fraction of solute; the fourth, the osmotic pressures calculated by the van 't Hoff equation; the fifth, those calculated by the equation of Morse and Frazer; the sixth, those calculated by Equation 7; the seventh, Morse and Frazer's observed values.

While the values given by the equation of van 't Hoff differ from those observed by nearly 25 per cent at the higher concentrations, it will be seen that the pressures given in the fifth and sixth columns agree throughout with the observed values, within the limits of experimental error, and differ from each other by only 1 per cent even at normal concentration.

This agreement between the osmotic pressures calculated from the equation of Morse and Frazer and those

calculated by Equation 7 will always be found at moderate concentrations, as the following considerations show. The second term in Equation 7, except at the very highest concentrations, is comparatively insignificant, amounting usually to only a few per cent of the value of Π even when the osmotic pressure is as high as a 1000 atmospheres. At moderate concentrations we may therefore neglect this term and write Equation 7 in the form—

$$\Pi = - \frac{RT}{V_0} \ln (1 - N_1) \dots \dots \dots 8,$$

Now the equation of Morse and Frazer may be written in the form—

$$\Pi = \frac{RT}{V_0} \left(\frac{N_1}{1 - N_1} \right) \dots \dots \dots (9),$$

for $\frac{N_1}{1 - N_1}$ is the number of mols. of solute to one mol. of solvent and V_0 is the volume of one mol. of pure solvent.

Equation 8 developed in series gives—

$$\Pi = \frac{RT}{V_0} \left(N_1 + \frac{1}{2} N_1^2 + \frac{1}{3} N_1^3 + \dots \right)$$

and, similarly, Equation 9 gives—

$$\Pi = \frac{RT}{V_0} \left(N_1 + N_1^2 + N_1^3 + \dots \right).$$

These equations differ only in the higher powers of N_1 , and therefore give identical results at such concentrations that the terms containing these higher powers are negligible. When the mol. fraction of the solute is 0.02 the values of Π calculated from these equations differ by 1 per cent. For all more dilute solutions, therefore, the osmotic pressure of a perfect solution may be calculated within 1 per cent from the equation of Morse and Frazer.

At higher concentrations, however, the difference between these two equations becomes very great, as is shown in Tables V. and VI. Table V. deals with solutions of ethylene chloride in benzene, and simply re-states in a new way the facts brought out in Table III. Table VI. contains data on solutions of propylene bromide in ethylene bromide. In both tables the first column gives the mol. fraction of solute; the second, the partial vapour pressure of the solvent, taken from the work of Zawidski (omitting the values which the author marks as questionable); the third, the osmotic pressure calculated by the van 't Hoff equation; the fourth, that calculated by the equation of Morse and Frazer; the fifth, that calculated by Equation 7, while the last column gives the actual osmotic pressure obtained thermodynamically from the vapour pressures by means of Equation 3. The molecular volumes of benzene and ethylene chloride at 50° are taken, respectively, as 0.092 and 0.082 litre, and the coefficient of compressibility of benzene as 0.0001. The molecular volumes of ethylene and propylene bromides at 85° are taken, respectively, as 0.092 and 0.113 litre, and the coefficient of compressibility of ethylene bromide as 0.00006.

We see from these tables how closely in these two cases the actual osmotic pressures agree with those calculated by Equation 7, and how far from the truth are the pressures calculated both by the van 't Hoff equation and by that of Morse and Frazer. These two solutions are, according to our definition, perfect solutions, within the limits of experimental error, for all concentrations from 0 to over 90 per cent of solute. Since, moreover, these cases are not unique but have been chosen out of a large number of similar cases merely because of the greater experimental care with which they have been investigated, it is to be presumed that even those solutions which are not perfect at all concentration will, on the average, follow the law expressed in Equation 7 to higher concentrations than they will the law of van 't Hoff or that of Morse and Frazer.

In view of the experiments of Morse and Frazer, it has recently been proposed that in the ordinary equations of chemical equilibrium the concentrations expressed in the

* From the *Journal of the American Chemical Society*, xxx., No. 5.

TABLE IV.

Concentration, weight normal.	Concentration volume normal.	Mol. fraction of solute.	Π van't Hoff.	Π Morse and Frazer.	Π Lewis.	Π observed.
0.1	0.098	0.00180	2.34	2.41	2.41	2.40
0.2	0.192	0.00358	4.58	4.81	4.80	4.74
0.3	0.282	0.00537	6.73	7.23	7.21	7.23
0.4	0.369	0.00715	8.81	9.64	9.60	9.67
0.5	0.452	0.00892	10.8	12.0	12.0	12.1
0.6	0.532	0.0107	12.7	14.5	14.4	14.4
0.7	0.610	0.0124	14.5	16.8	16.7	16.9
0.8	0.684	0.0142	16.3	19.3	19.2	19.4
0.9	0.756	0.0159	18.1	21.7	21.5	21.8
1.0	0.825	0.0177	19.7	24.1	23.9	24.5

TABLE V.

C₂H₄Cl₂ in C₆H₆ at 50°.

N ₁ .	p ₂ .	Π van't Hoff.	Π Morse and Frazer.	Π Lewis.	Π found.
0.0	268.0	—	—	—	—
0.293	189.8	91	120	101	100
0.416	156.0	128	205	157	158
0.522	127.8	160	315	215	217
0.657	92.4	196	549	313	310
0.754	65.9	223	880	413	406
0.920	21.8	268	3290	743	735

TABLE VI.

C₃H₆Br₂ in C₂H₄Br₂ at 85°.

N ₁ .	p ₂ .	Π van't Hoff.	Π Morse and Frazer.	Π Lewis.	Π found.
0.0	172.6	—	—	—	—
0.147	145.1	47	55	51	55
0.222	132.2	69	91	80	86
0.298	121.1	90	136	113	114
0.412	101.1	121	224	171	173
0.526	81.9	150	351	241	240
0.620	64.0	173	520	313	319
0.720	48.0	198	820	412	414
0.800	34.3	218	1280	522	525
0.860	23.5	232	1960	640	649
0.915	13.8	241	3440	806	827

volume normal system should be replaced by those expressed in the weight normal system (Walden, *Zeit. Phys. Chem.*, lviii., 500; this paper also contains a letter from van't Hoff on this subject). This is undoubtedly an improvement, but the equations thus obtained are not entirely correct, even when all the substances concerned are present as perfect solutions.

In order to find an exact equation, let us consider a reaction occurring as follows:—



where x_1 mols. of X_1 combine with x_2 mols. of X_2 to form x_3 mols. of X_3 , &c. It is readily seen from the considerations advanced in this paper and from the thermodynamic laws of chemical equilibrium (Lewis, *loc. cit.*, Equation XXIII.), that the general equation of chemical equilibrium, regardless of the concentrations of the reacting substances, provided that they are all present as perfect solutions, is as follows:—

$$\frac{N_3^{x_3} N_4^{x_4} \dots}{N_1^{x_1} N_2^{x_2} \dots} = K \text{ (a constant) } \dots \text{ to ;}$$

where N_1 , N_2 , &c., are the respective mol. fractions of X_1 , X_2 , &c.

This, then, is the form which the mass law assumes when the substances concerned form perfect but not infinitely dilute solutions, and for such cases it is rigorously exact.

(To be continued).

FURTHER INVESTIGATION OF THE ATOMIC WEIGHTS OF NITROGEN AND SILVER.*

By THEODORE WILLIAM RICHARDS, PAUL KÖTHNER,
and ERICH TIEDE.

(Continued from p. 56).

The Final Preparation and Weighing of Ammonium Chloride.—The ammonium chloride, as prepared by the methods described in the preceding section, was exceedingly pure, except from the presence of water and the doubt as to whether the substance had attained exact neutrality. These two doubts, however, would be enough to vitiate the whole work, provided that they were not removed—for the presence of water is just as serious, weight for weight, as the presence of any other substance; and it would be indeed foolish to spend much thought on eliminating traces of sodium, for example, while leaving much larger weights of water in the final material. Again, an excess of ammonia or hydrochloric acid would have an equally pernicious effect upon the results. The presence of either would obviously be very much worse than the presence of equal amounts of sodium chloride.

Taking this into account, it was obviously necessary to dry thoroughly the ammonium chloride, and sublime it in such a way as to insure, as definitely as possible, the

* *Journal of the American Chemical Society*, xxxi., No. ,

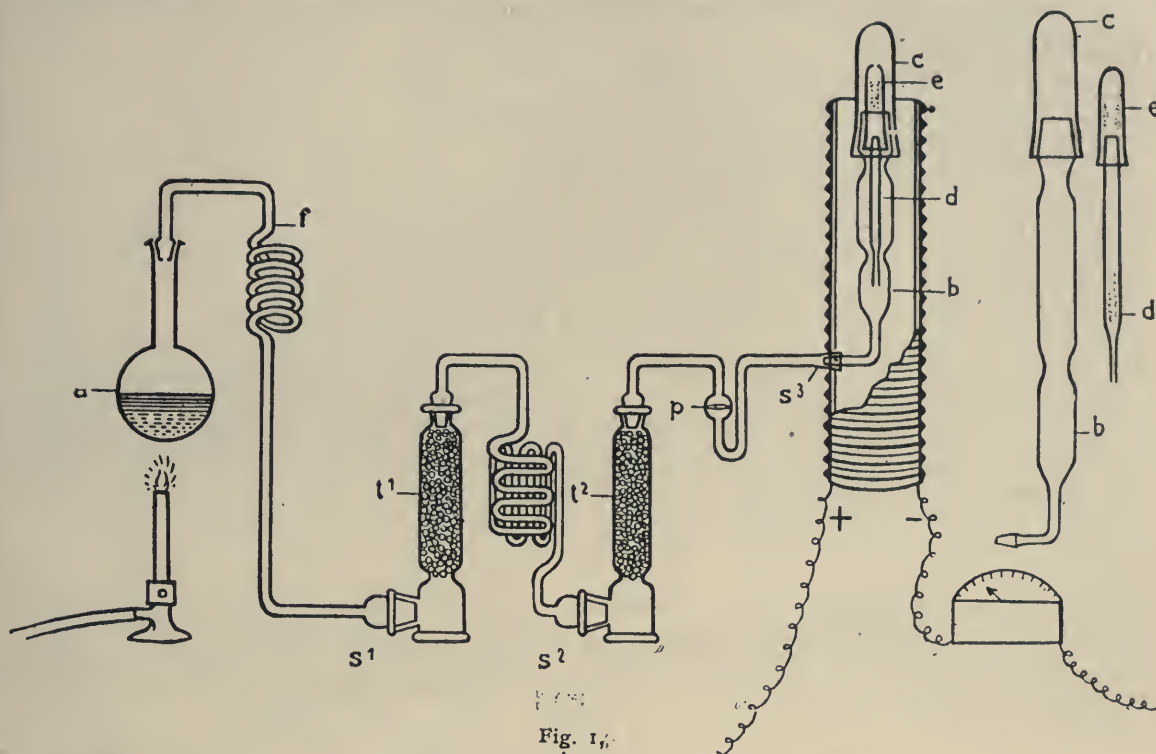


Fig. 1.

proper proportion of acid and volatile alkali. Ammonium chloride is an especially convenient substance to use as the basis of an atomic weight determination, because it is

so easily sublimed. In this way it may be purified, and, moreover, an admirable test is furnished by sublimation, enabling one to determine whether or not non-volatile impurities are eliminated. Unfortunately, however, as is well known, the substance ordinarily sublimes by transition into a dissociated state, and the experimenter can never be certain that during the sublimation in another gas a portion of the lighter gas, ammonia, has not escaped, because of its more rapid diffusion. Sublimation brings with it a further difficulty common to most cases of the kind, namely, dangerous interaction between hot gases and the vessels in which the operation must be conducted. Hence, although sublimation furnishes an admirable means of leaving behind non-volatile impurities, it must be used with caution, especially in this particular case.

Turning first to the latter cause of danger, we found by preliminary experiments that for this purpose both hard glass and platinum are unsuitable—each being attacked sufficiently to endanger the purity of the product. On the other hand, repeated experiments proved that fused quartz is entirely resistant to ammonium chloride, ammonia, and hydrochloric acid at the temperatures needed in the present work, and accordingly it alone was used wherever ammonium chloride came in contact with the containing vessel. (We take this opportunity for thanking the firm of Heraeus in Hanau for their kindness in furnishing some of the quartz apparatus with great promptness at one crisis in the experimentation).

The best method of avoiding the former cause of uncertainty and inexactness seemed to be the following:—Every sample of ammonium chloride was sublimed twice, once in a current of ammonia gas in order to prevent the possibility of the existence of free acid, and again in a Sprengel vacuum in order to insure the elimination of the extra ammonia.

The three quartz tubes used for the double sublimation were shaped in such a way that the first yielded its product into the second, and the second yielded its product into the

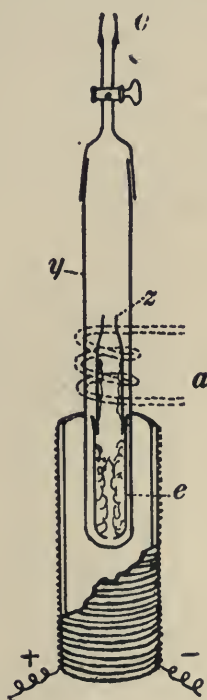


Fig. 2.

third, which in turn could be used directly for the weighing of the preparation.

The difference in treatment involved different apparatus in the two cases. For sublimation in a current of ammonia the apparatus shown in Fig. 1 was employed. In *a* was placed a concentrated solution of calcium chloride saturated with the purest ammonia gas. By heating this solution a continuous stream of fairly dry ammonia gas may be obtained. This was further dried by means of purest lime in towers *t*¹ and *t*². Cotton-wool in the upper stopper of the second tower served to hold back powdered lime which might have been swept along, and at *p* was a glass tube containing a porous porcelain diaphragm filter—according to Stock (*Ber.*, 1907, xl, 4956). The complete absence of dust was found to be necessary in order to prevent contamination of the product. Hence these special precautions were taken, and, moreover, the complete elimination of rubber connections was effected by fusing or grinding the tubes together.

The substance to be sublimed was placed in a small tube, *d* (shown also on a larger scale on the right-hand side of the figure), and upon this tube was placed a somewhat larger glass tube *b* which was heated by means of a suitable magnesia tube wound with resistance wire. The excess of ammonia which flowed through the apparatus during the sublimation escaped from the small hole at the top of *e*.

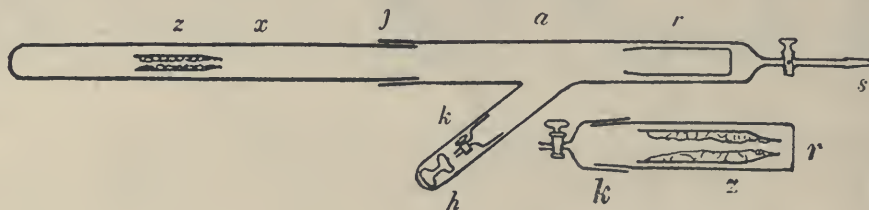


FIG. 3.

It was easily possible to regulate the sublimation so that most of the solid material deposited within the quartz tube *e*, for the condensation occurs in the zone just beyond the hotter part of the tube, as the preliminary experiments had demonstrated.

The final purification by sublimation in a vacuum took place immediately after this by fitting into the tube (*e*), after it had been removed from the apparatus just described, a third quartz tube, named *z* in Fig. 2. This was of a projectile-like shape, open at both ends, and small enough to fit into the weighing bottle, which formed its final resting place.

The arrangement of the apparatus for the second sublimation is shown in Fig. 2, its form having been devised by degrees with the help of many unsuccessful attempts. The tubes containing the ammonium chloride, *e* and *z*, were placed in a larger tube, *y*, made of the hardest Jena glass. This larger tube was closed above with a ground glass cup, provided with a glass stopcock for connecting with a mercury air-pump. After the complete exhaustion of the tubes, the sublimation was conducted with the help of the electric heater. A lead tube with running water cooled the sublimate, so that a sufficient amount of it was deposited on the inner wall of *z*. Prepared in this way ammonium chloride deposits itself in beautiful diamond-like crystals, which become clouded only upon cooling, and are then pure white. No residue was left in the tube *e*. All the material used in the analyses was sublimed twice in this way.

Stas has shown that ammonium chloride gains more weight when it is weighed in a vacuum than would be expected from its weight in air and its specific gravity. He found that 1 gm. of ammonium chloride under ordinary atmospheric conditions weighs +0.00080 more in a vacuum than in air (Stas, "Untersuchungen," Aronstein's translation, 1867, p. 56). The present experience entirely sup-

ports this value, and it is worth while now to describe the apparatus by which the conclusion was tested. This apparatus was a modification of the familiar bottling apparatus which has served for so many researches in Harvard University. In the present case the apparatus was modified for use in a vacuum, and the details are sketched in Fig. 3. The projectile-shaped boat or receptacle *z*, filled with ammonium chloride in the manner just described, was placed in a hard glass tube, *x*. This in turn was ground into a tube similar to the familiar bottling apparatus except that its side excrescence was elongated so as to contain a small glass hammer as well as the cap-stopper of the weighing tube *r*. After the air had been wholly removed, the apparatus was disconnected from the pump and tilted. Thus the ammonium chloride with its container, *z*, was allowed to glide into the weighing bottle, *r*, and the cap, already carefully provided inside with a thin film of lubricant, was allowed to fall into place. The weighing bottle was finally securely closed by means of gentle blows of the small glass hammer *k*. It was customary to heat the ammonium chloride almost to sublimation before disconnecting the pump. When the weighing bottle was effectually sealed, dry air was admitted to the apparatus, and the weighing bottle removed to the desiccator and weighed at leisure. Afterwards dry air was admitted and the tube was weighed again later; when the

ammonium chloride had been dissolved away, the weighing bottle and quartz container were exhausted in a similar way and once more weighed, both evacuated and filled with air, using the same closed counterpoise in each case. Thus the weight of ammonium chloride in vacuum was determined directly, and the vacuum correction could be easily calculated. After Stas's vacuum correction had been verified, time was saved for many of the analyses by simply weighing the ammonium chloride in air by means of the usual bottling apparatus without the additional heating and confining in a vacuum.

(To be continued.)

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 1st instant, Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, in the Chair. Mr. W. E. Lake, Dr. A. Liversidge, Dr. K. C. E. von Martius, and Mr. F. J. Sharpe were elected Members. The Treasurer announced that the sum of £10,000 had been anonymously and unconditionally placed at the disposal of the Managers for the purposes of the Institution by a lady; and the Members passed a resolution expressing their most grateful appreciation of her munificence and discernment, accepting the gift as a timely and noble recognition of the good public works the Institution has done in the past, and is still doing, in the acquisition and diffusion of scientific knowledge, and as an incitement to maintain and extend its usefulness in the unique position which it has for more than a century occupied. The Honorary Secretary reported the decease of Dr. Francis Elgar, F.R.S., a late Manager, and a Resolution of Condolence with the family was passed.

PROCEEDINGS OF SOCIETIES

CHEMICAL SOCIETY.

Ordinary Meeting, January 21st, 1909.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President,
in the Chair.

THE minutes of the previous meeting having been read and confirmed, Dr. DIVERS made the following inquiries:—Whether one of the objects of the resolution adopted by the Council "to remove some of the disabilities experienced by women chemists" were not, as it appeared to be, to let duly qualified women be "accepted" to enjoy privileges in the Society which men, similarly qualified, were not to be permitted to enjoy on the same terms, and, that being so, whether that object was a just and lawful one? Whether the Council, in taking upon itself to "enact a regulation" (Charter, p. 6) indistinguishable in form and substance from a by-law, had avoided exceeding its powers merely by not proceeding to call the regulation a by-law? In what did the resolution concerning Subscribers of the Society differ from the existing by-law for Associates, except in that an Associate must have passed a ballot of the Fellows? Was it not clear from the Charter that any action by the Council on the resolution would be invalid until the vote of a General Meeting should have made the resolution into a by-law? Whether the Council must not be exceeding its powers in legislating for women in any way whatever, if it were indeed the case that it would be going beyond its powers were it to accept women as candidates for the Fellowship, they being, it was said, outside the consideration of the Charter? Would not even a General Meeting be exceeding its much greater powers were it to attempt to frame quasi-by-laws for those to whom the Charter did not apply? Did the Council in its words "disabilities experienced by women" refer to its assumption that the Charter really imposed upon it disability to receive the candidature of women for the Fellowship? If so, did it need to be pointed out that disabilities, like any other ordinances, were not "experienced" by anyone, but were imposed, and that a Charter did not attempt to limit the powers of any man or woman who was not enjoying the privileges which it bestowed? In speaking of "removing disabilities" did the Council maintain that it could itself escape from or could relieve others of a disability laid upon it or upon them by the Charter? Lastly, was it to be understood that the Council believed, what its words implied, that it would be removing disabilities by granting privileges, supposing that it really could do either of these things?

Messrs. N. C. Akers, J. Brown, R. F. Easton, C. Everitt, A. F. Girvan, C. L. Norman, G. E. Pearson, W. B. Shaw, W. G. Winterson, and F. P. Worley were formally admitted Fellows of the Society.

THE PRESIDENT announced a proposal by the Institution of Gas Engineers to perpetuate the memory of the late Sir George Livesey by establishing a Livesey Professorship in Gas Engineering and Fuel at the Leeds University; contributions to the Fund should be addressed to the Secretary of the Institution of Gas Engineers, 39, Victoria Street, Westminster.

Certificates were read for the first time in favour of Messrs. Alfred Bertram Coles, M.A., 42, Broadwater Road, Tottenham, N.; John Thomas Fox, Glen Burn, Stollard Street, Clay Cross, near Chesterfield; John Thomas Furnell, 32, Grosvenor Park Road, Walthamstow; Alfred George Cooper Gwyer, Ph.D., B.Sc., Keate House, Durham Down, Bristol; Robert Main Harland, 296, Willesden Lane, Willesden Green, N.W.; Henry Humphreys Jones, 18, Colquit Street, Liverpool; Horace Keeble, Wereham, Stoke Ferry, Norfolk; Joseph Leedham, 176, Bromford Lane, West Bromwich; William

George Martin, B.Sc., Royal School, Armagh; Robert Robinson, M.Sc., Field House, Chesterfield; Herbert Rogers, Stenning House, Cobwell Road, Retford, Notts; J. H. Charles Schulten, Ph.D., 4, Pollock Street, Calcutta; Guy Ransom Warwick, B.A., 5 and 6, Fowkes Buildings, Great Tower Street, E.C.; Percy Charles Henry West, 40, The Green, Norton, Co. Durham; Thomas Jabez Wild, Scott's Laboratories, Southall, Middlesex.

The Council has ordered the following letter and report to be printed in the *Journal* and *Proceedings* of the Society:—

Government Laboratory,
Clement's Inn Passage, Strand, London, W.C.,
October 29th, 1908,

GENTLEMEN,—I beg to forward you, for presentation to the Council of the Chemical Society, the Report of the International Committee on Atomic Weights, 1909, to which I have affixed, as desired by them, the signatures of Professors Ostwald and Urban.

The general revision of the values of the atomic weights of the elements, based on the fundamental values for hydrogen, nitrogen, the halogens, silver, &c., as ascertained by the laborious and accurate determinations which have been made in various laboratories during recent years, and to which reference was made in preceding Reports, has now been completed and the Table submitted with the present Report embodies the results of the re-calculations. A number of atomic weights are shown to be slightly influenced by the adoption of the new values, but the changes thus introduced are, it must be admitted, less profound than was generally anticipated. Certain of the values still remain affected by errors far larger than those introduced by the selection of a particular fundamental value of the element with which comparison is made.—I am, Gentlemen, your obedient Servant,

T. E. THORPE.

The Hon. Secretaries, The Chemical Society,
Burlington House, London, W.

Report of the International Committee on Atomic Weights, 1909.

Since the publication of our last Report, several important memoirs upon atomic weights have appeared containing data of fundamental significance. They may be summarised as follows:—

Hydrogen.—W. A. Noyes (*Journ. Am. Chem. Soc.*, 1907, xxix., 1718) has made complete syntheses of water in five series of determinations. The first series, however, was defective, and is therefore not published by the author. In mean, the four successful series give $H = 1.00787$, as compared with Morley's figure, 1.00762 . The general mean of these values, combined with all other trustworthy determinations, is 1.00779 . The rounded-off value, 1.008 , is therefore retained in the table.

Chlorine.—Noyes and Weber (*Journ. Am. Chem. Soc.*, 1908, xxx., 13) have effected the synthesis of hydrochloric acid, weighing the hydrogen in palladium, the chlorine in potassium chloroplatinate, and also the hydrochloric acid produced by the union of the two elements. From the ratio $H:Cl$, $Cl = 35.458$, when $H = 1.00779$. From the ratio $H:HCl$, $Cl = 35.457$.

The same ratios have also been measured by Edgar (*Proc. Roy. Soc.*, 1908, lxxxi., A, 216), but by a different method. The hydrogen, as in former determinations, was weighed in palladium, but the chlorine was prepared by the electrolysis of fused silver chloride, and weighed in the liquid form. The hydrogen chloride was weighed directly in three experiments, and in two others after absorption in water. From the ratio $H:Cl$, $Cl = 35.468$. From the ratio $H:HCl$, $Cl = 35.467$. With Morley's value for H , the results are nearer $Cl = 35.46$. Taking all the data together, the value $Cl = 35.46$ seems to be as near the truth as can be positively asserted now. This includes the former work of Dixon and Edgar, and the density determinations by Guye and Gazarian.

Sulphur (private communication from Prof. P. A. Guye).—From eighteen determinations of the density of hydrogen sulphide, Baume and Perrot deduce the value $S=32.070$. In an earlier investigation by Baume (*Journ. Chim. Phys.*, 1908, vi., 1), who determined the density of sulphur dioxide, he found lower values for S. (Baume also determined the densities of methyl oxide and methyl chloride). The figure 32.07, however, is in close agreement with the value obtained by Richards and Jones, when $Ag=107.88$, and is doubtless very nearly true.

Lead.—Atomic weight determined by Baxter and Wilson (*Proc. Amer. Acad.*, xliii., 365) from analyses of the chloride. With $Ag=107.93$, $Pb=207.19$. With $Ag=107.88$, $Pb=207.10$. This value is still much higher than that previously accepted.

Cadmium.—Blum (Thesis, University of Pennsylvania, 1908) has attempted to determine the atomic weight of cadmium by conversion of the oxide into the sulphide. The values obtained range from 112.50 to 112.88, and are admittedly of slight significance.

Tellurium.—In an elaborate memoir upon the atomic weight of tellurium, Baker and Bennett (*Trans.*, 1907, xci., 1849) give determinations by two new methods. By heating tellurium dioxide with sulphur in such a way that only sulphur dioxide could escape, the ratio TeO_2 to SO_2 was determined. From the mean of twenty-five determinations, $Te=127.609$. By direction conversion of tellurium into the tetrabromide, the mean of eighteen determinations was $Te=127.601$, when $Br=79.96$. Referred to $Br=79.92$, this becomes 127.54. Several analyses of tellurium tetrachloride, for which the details are not published, gave values for Te between 127.58 and 127.64. On the basis of the modern values for Ag, Cl, and Br, and with due regard to the earlier work of Pellini, Gutbier, Koethner, Norris, Scott Staudenmaier, and others, the rounded-off figure, $Te=127.5$, seems to be fairly acceptable.

Marckwald (*Ber.*, 1907, xl., 4730), however, by careful dehydration of telluric acid, found values for Te ranging from 126.65 to 126.94. (For a criticism of Marckwald, see Baker, *CHEMICAL NEWS*, 1908, xcvi., 209). Six experiments were made, the mean of five, rejecting the lowest of all, being $Te=126.85$. This falls below the atomic weight of iodine, and is therefore in harmony with the periodic classification. In view of the general agreement between other investigators in favour of a higher figure, Marckwald's work cannot be accepted without confirmation. The controversy over tellurium is evidently not ended.

Rhodium.—Huttlinger (*Diss.*, Erlangen, 1907), working in Gutbier's laboratory, made three reductions in hydrogen of rhodium pentamine chloride. His results, which seem to be preliminary in character, are practically identical with those obtained by Seubert and Kobbe, whose value for rhodium has been accepted since 1890. No change in this atomic weight is needed.

Palladium.—Woernle (*Sitzungsber. Phys. Med. Soz. Erlangen*, xxxviii., 296) made seven analyses of palladosamine chloride; two by reductions in hydrogen, three electrolytically. The mean value obtained was $Pd=106.708$, presumably computed with the old figures for N and Cl.

Haas (*Diss.*, Erlangen, 1908), from similar reductions of palladosamine bromide, found $Pd=106.75$, calculated with $N=14.037$ and $Br=79.953$. These determinations, like those of Krell, were made under the direction of Prof. Gutbier. The results obtained by Krell, Woernle, and Haas agree well together, and also with Amberg's determinations, and are probably quite accurate. Re-computed, with modern values for N and Cl, $Pd=106.7$ very nearly, with an uncertainty of not over 0.05.

Lower values were found by Kemmerer (Thesis, University of Pennsylvania, 1908), working under Prof. Edgar F. Smith. By reduction in hydrogen, palladosamine chloride gave $Pd=106.399$ and 106.442 as the means of two series of observations. From palladosamine cyanide the value $Pd=106.458$ was obtained. The mean of fifteen determinations, taken as one series, gave $Pd=106.434$.

The more concordant values cited above seem to be more trustworthy, at least so far as present evidence permits us to judge. Kemmerer's computations were made with $N=14.01$ and $Cl=35.473$.

Europium.—From analyses of the octahydrated sulphate, Jantsch (*Comptes Rendus*, 1908, cxlvi., 473) finds $Eu=152.03$, when $S=32.06$ and $H=1.008$. The round number 152 is retained in the table. This is probably the nearest significant figure.

Erbium.—By repeated fractionation of erbium compounds Hofmann and Berger (*Ber.*, 1908, xli., 308) have isolated an oxide of slightly higher molecular weight than that of the old erbia. To the new metal thus indicated they assign the name "neo-erbium," and by synthesis of the sulphate they find its probable atomic weight to be 167.43. The rounded-off figure 167.4 is given provisionally in the table, to stand until more complete data have been obtained.

Ytterbium.—That the old ytterbium is a mixture of two elements has been proved by Urbain (*Comptes Rendus*, 1907, cxlv., 759, November 4, 1907; see also *Comptes Rendus*, 1908, cxlvi., 406, and *Chem. Zeit.*, 1908, xxxii., 730), in Paris, and Auer von Welsbach, in Vienna (*Monatsh.*, Feb., 1908, xxix., 181; read before the Vienna Academy, Dec., 1907), working almost simultaneously and independently. In his earlier paper, Urbain names the two elements "neoytterbium" and "lutecium," with approximate atomic weights of 170 and 174 respectively. In his second memoir, Urbain gives atomic weights for a series of ytterbium fractionations, ranging from 170.6 to 174.02. Welsbach, whose work appeared later than Urbain's, names the two elements "aldebaranum," atomic weight 172.90, and "cassiopeium," atomic weight 174.23. Since Urbain has clear priority, his nomenclature should be preferred, but the atomic weights need to be more sharply determined. Incidentally, Urbain notes that the atomic weight of thulium is lower than 168.5.

Columbium.—A concordant series of determinations made under the direction of Edgar F. Smith give columbium an atomic weight of 93.5 (Private communication; the details are shortly to be published). This is lower than the value hitherto accepted.

Radium.—Thorpe (*Proc. Roy. Soc.*, 1908, lxxx., A, 298) has re-determined the atomic weight of radium by analyses of the chloride. In mean his determinations, calculated with $Ag=107.88$ and $Cl=35.46$, give $Ra=226.64$. Thorpe, however, gives preference to the determinations by Mme. Curie, who worked with larger quantities of material, regarding his own work as confirmatory. The re-calculated value is 226.4.

In their Report for 1908, this Committee recognised the fact that a general revision of the atomic weight table was desirable, and such a revision has now been made. Modern investigations have shown that the fundamental values required modification, and through them many other atomic weights are affected, although the changes thus brought about are less important than they were generally supposed to be. Many atomic weights remain practically unaltered, and in few instances are the changes large, as a comparison of the new table with its predecessors will show. A careful scrutiny of all the evidence was, however, none the less necessary, and the table now offered gives the results thus obtained.

The fundamental atomic weights, the standards of reference employed in the calculations, are as follows; when $O=16$:—

H	1.008	Br	79.916
C	12.00	Ag	107.880
N	14.007	K	39.095
Cl	35.460	S	32.070

The value for silver is possibly a trifle too low, by from three to five units in the third decimal place. A combination of the best measurements gives $Ag=107.883$. In this case, and in others as well, the second place of decimals is given in the table, the third place being

uncertain. Thus we have K, 39.10; N, 14.01; Br, 79.92; &c. Only with hydrogen is the third place retained.

In adjusting the other atomic weights, the determinations by Richards and his colleagues have generally been given preference. (An excellent summary of the Harvard work is given by Richards in *Journ. Chim. Phys.*, 1908, vi., 92). They are certainly entitled to the highest weight, but probably not to exclusive consideration. The work of Guye and his associates at Geneva, and the recent direct measurements of the chlorine-hydrogen ratio are also of very great importance. It is to work of this order that we must look for ultimate precision. Important investigations upon atomic weights are now being carried out in several laboratories, and our knowledge of these constants will doubtless become much more exact within the near future.

(Signed) F. W. CLARKE,
W. OSTWALD,
T. E. THORPE,
G. URBAIN.

International Atomic Weights. (1909).

(O = 16).

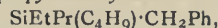
Aluminium	Al	27.1
Antimony	Sb	120.2
Argon	A	39.9
Arsenic	As	75.0
Barium	Ba	137.37
Bismuth	Bi	208.0
Boron	B	11.0
Bromine	Br	79.92
Cadmium	Cd	112.40
Cæsium	Cs	132.81
Calcium	Ca	40.09
Carbon	C	12.00
Cerium	Ce	140.25
Chlorine	Cl	35.46
Chromium	Cr	52.1
Cobalt	Co	58.97
Columbium	Cb	93.5
Copper	Cu	63.57
Dysprosium	Dy	162.5
Erbium	Er	167.4
Europium	Eu	152.0
Fluorine	F	19.0
Gadolinium	Gd	157.3
Gallium	Ga	69.9
Germanium	Ge	72.5
Glucinum	Gl	9.1
Gold	Au	197.2
Helium	He	4.0
Hydrogen	H	1.008
Indium	In	114.8
Iodine	I	126.92
Iridium	Ir	193.1
Iron	Fe	55.85
Krypton	Kr	81.8
Lanthanum	La	139.0
Lead	Pb	207.10
Lithium	Li	7.00
Lutecium	Lu	174
Magnesium	Mg	24.32
Manganese	Mn	54.93
Mercury	Hg	200.0
Molybdenum	Mo	96.0
Neodymium	Nd	144.3
Neon	Ne	20
Nickel	Ni	58.68
Nitrogen	N	14.01
Osmium	Os	190.9
Oxygen	O	16.00
Palladium	Pd	106.7
Phosphorus	P	31.0
Platinum	Pt	195.0
Potassium	K	39.10
Praseodymium	Pr	140.6

Radium	Ra	226.4
Rhodium	Rh	102.9
Rubidium	Rb	85.45
Ruthenium	Ru	101.7
Samarium	Sa	150.4
Scandium	Sc	44.1
Selenium	Se	79.2
Silicon	Si	28.3
Silver	Ag	107.88
Sodium	Na	23.00
Strontium	Sr	87.62
Sulphur	S	32.07
Tantalum	Ta	181.0
Tellurium	Te	127.5
Terbium	Tb	159.2
Thallium	Tl	204.0
Thorium	Th	232.42
Thulium	Tm	168.5
Tin	Sn	119.0
Titanium	Ti	48.1
Tungsten	W	184.0
Uranium	U	238.5
Vanadium	V	51.2
Xenon	Xe	128
Ytterbium (Neoytterbium)	Yb	172
Yttrium	Y	89.0
Zinc	Zn	65.37
Zirconium	Zr	90.6

Of the following papers those marked * were read:—

*1. "Organic Derivatives of Silicon. Part IX. Experiments on the Resolution of dl-Benzylethylpropylisobutylsilicanesulphonic Acid." By FREDERIC STANLEY KIPPING and HAROLD DAVIES.

dl-Benzylethylpropylisobutylsilicane—



a liquid boiling at 282—283°, has been prepared by treating benzylethylpropylsiliclyl chloride (Kipping, *Trans.*, 1907, xci., 717) with magnesium isobutyl bromide; when treated with chlorosulphonic acid, it gives a monosulphonic derivative, which is isolated in the form of its l-menthylamine salt.

l-Menthylamine dl-benzylethylpropylisobutylsilicanesulphonate, $\text{SiEtPr}(\text{C}_4\text{H}_9)_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5\cdot\text{SO}_3\text{H}\cdot\text{C}_{10}\text{H}_{21}\text{N}\cdot 2\text{H}_2\text{O}$, separates from moist light petroleum in lustrous leaflets, and, when dehydrated, melts at 127—128°; it is very similar in its properties to the corresponding salts of benzylmethylethylpropylsilicanesulphonic acid (*loc. cit.*) and of benzylethylidipropylsilicanesulphonic acid (Marsden and Kipping, *Trans.*, 1908, xciii., 205), although the latter is not a dl-compound.

The *strychnine*, *brucine*, *cinchonidine*, *quinine*, and *cinchonine* salts of the dl-acid and the corresponding hydrogen alkaloidal salts of the last-named three bases have been prepared; these eight compounds were systematically crystallised under various conditions, but in all cases, except in that of the cinchonine hydrogen salt, the melting- or decomposing-points and the specific rotations of the extreme fractions of a given salt were identical. The cinchonine hydrogen salt gave fractions having the same decomposing-points, but differing widely in specific rotation; whether this difference is due to a resolution of the acid or not is still an open question.

*2. "The Crystallisation of Externally Compensated Mixtures." By FREDERIC STANLEY KIPPING and WILLIAM JACKSON POPE.

The recent publication of Ostromisslensky's paper (*Ber.*, 1908, xli., 3035) on this subject affords an occasion for briefly recording the results of some work commenced in 1898, but which has not been brought to a definite issue.

On crystallising dl-sodium ammonium tartrate (prepared from purified racemic acid) from aqueous solutions of dextrose, and then re-crystallising the deposit, the product consisted, in nearly all cases, of the d-tartrate, almost or entirely free from the l-salt (*Proc.*, 1898, xiv., 113).

It is now shown that similar results are obtained in absence of dextrose even when the racemic acid, used in the preparation of the sodium ammonium salt, has been repeatedly crystallised from water. This preferential deposition of the *d*-tartrate may be due to the seeding of the solutions by laboratory dust, or to the presence of a minute excess of the *d*-acid in the racemic acid employed; the results obtained on fractionally crystallising commercial racemic acid itself seem to show that the complete removal of extremely small quantities of dextrorotatory impurity is a very difficult matter.

*3. "Formation of cyclohexanone Derivatives from Olefinic Compounds." By SIEGFRIED RUHEMANN.

Although the esters of acetylenic acids form additive products with phenols, olefinic monocarboxylic esters or olefinic monoketones do not unite with sodium phenoxide. Condensation, however, takes place if the number of electronegative groups in an olefinic compound is increased. The additive compound of ethyl benzylideneacetoacetate with sodium phenoxide at once condenses, thus—

$$2\text{CHPh}(\text{OPh})\cdot\text{CHAc}\cdot\text{CO}_2\text{Et} = \text{C}_{26}\text{H}_{28}\text{O}_6 + 2\text{C}_6\text{H}_5\cdot\text{OH},$$

yielding a compound, $\text{C}_{26}\text{H}_{28}\text{O}_6$, which has twice the molecular formula of ethyl benzylideneacetoacetate. The substance is regarded as a cyclohexanone derivative, $\text{CO}_2\text{Et}\cdot\text{C}\text{Ac}\text{C}(\text{CHPh})_2\text{CH}(\text{CO}_2\text{Et})\text{CH}_2\text{CO}$, and this constitution is supported by a number of facts which the closer study of the reaction has furnished.

Similar cyclohexanone derivatives have been obtained by the action of sodium phenoxide on benzylideneacetylacetone, $\text{CHPh}\cdot\text{C}\text{Ac}_2$, and ethyl ethylideneacetoacetate, $\text{CHMe}\cdot\text{C}\text{Ac}\cdot\text{CO}_2\text{Et}$.

On the other hand, but in harmony with the above view of the formation of these cyclohexanone compounds, neither ethyl benzylidenemalonate, $\text{CHPh}\cdot\text{C}(\text{CO}_2\text{Et})_2$, nor ethyl benzylidenebenzoylacetate, $\text{CHPh}\cdot\text{CBz}\cdot\text{CO}_2\text{Et}$, condenses to cyclic compounds, although uniting with sodium phenoxide.

(To be continued).

NOTICES OF BOOKS.

Guide Pratique du Chimiste Métallurgiste et de l'Essayeur. ("Practical Guide for the Metallurgical Chemist and Assayer"). By L. CAMPREDON. Second Edition. Paris: Ch. Béranger. 1909.

THIS work contains detailed descriptions of various methods of analysis employed in metallurgy and assaying, together with in most cases sufficient information on their applicability to enable the chemist to come to a judicious decision as to which one to adopt in particular cases. The number of methods described, however, for a given constituent is often large, and occasionally a little more definite statements with regard to which one is most usually or satisfactorily employed might have been an advantage. The rare earths are included, and particular care has been taken to overlook no essential details of manipulation and to make the book a thoroughly practical laboratory guide; indeed, in some respects the author has carried his endeavours after completeness rather far, and there is some matter dealing with quite elementary processes and apparatus which might have been omitted without in any way diminishing the usefulness of the book.

Feste Lösungen und Isomorphismus. ("Solid Solutions and Isomorphism"). By Dr. GIUSEPPI BRUNI. Leipzig: Akademische Verlagsgesellschaft. 1908.

ONE of the easiest ways of getting a general idea of a branch of any scientific subject is to read a good lecture in

which in nearly all cases the matter is stated more simply and also more graphically than in an article. The truth of this general statement is well illustrated by this book, which is a reproduction with some extensions of a lecture delivered by Prof. Bruni before the Chemical Society at Breslau. The text is divided into numerous very short chapters, each one discussing some single point; many summaries are given, and as little mathematics as possible is introduced. The text is thus easy to follow, and, moreover, it gives a survey of the whole subject, details being avoided as far as possible. The lecture was divided into two parts, the first dealing with the nature of solid solutions, their methods of formation and most important properties, and the second giving a discussion of the disputed question of isomorphism in the light of recent advances. The relation between crystalline form and chemical constitution is well treated, and an ingenious table shows at a glance the behaviour of the elements, especially the metals, when they separate from mixed binary melts.

CORRESPONDENCE.

WOMEN AND THE FELLOWSHIP OF THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—It has come to our notice that a report has been widely circulated and credited to the effect that the movement in favour of the admission of women to the Fellowship of the Chemical Society is directly connected with the present agitation for the political enfranchisement of women. We, the undersigned women (actively engaged in chemical teaching and research), beg to ask for the hospitality of your columns in order to deny any such connection. The following facts, we venture to think, should prove the independence of the two movements:—

1. Five years ago when some of us petitioned the Council of the Chemical Society to admit us to the Fellowship, the agitation in favour of "Woman Suffrage" was not prominently before the public.

2. The petition recently presented to the Council originated within the Chemical Society itself, and was signed exclusively by Fellows of the Society.

Moreover, we, as a body, have no knowledge of the political opinions and aspirations held by individual members; any such knowledge we should consider to be quite irrelevant, since the only link which unites us is a common interest in the science of chemistry. We are glad to take this opportunity of recording our thanks to those Fellows of the Chemical Society who have expressed themselves in favour of admitting women to the Fellowship of the Society.—We are, &c.,

(Signed)

HEATHER H. BEVERIDGE, B.Sc., Carnegie Research Scholar, Univ. of Edinburgh.

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KATHARINE I. WILLIAMS.

Since the above was written the following letter has been sent to the signatories of the original petition:—

London, January 30, 1909.

DEAR SIR,—At a meeting of representative women chemists held on the 8th inst., a hearty vote of thanks was accorded to the 312 Fellows of the Chemical Society who presented the petition to the Council praying for the admission of women to the Fellowship. At the same meeting it was unanimously decided that it is not advisable for women to take advantage of the new regulation adopted by the Council whereby women are permitted to become "Subscribers." In conveying to you, as one of the signatories of the petition, our thanks for your efforts to obtain for us recognition of our claim to be admitted to the Fellowship, we wish to state that the above decision was reached only after careful consideration of its bearing on the fundamental question on which the petition and referendum were based. We are of opinion that by becoming Subscribers to the Chemical Society we should prejudice unfavourably the case for granting to women the Fellowship of the Society.—We are, &c.,

(Signed as above).

Impersonation.—A Warning.—Consulting and analytical chemists and others are again warned against receiving a tall seedy-looking man, who, on the plea of ill-health, solicits pecuniary or other assistance by impersonating a certain Fellow of the Institute of Chemistry in practice at Warrington.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

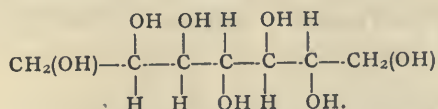
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvii., No. 26, December 28, 1908.

Law of the Optimum of Cathode Phosphorescence of Binary Systems.—G. Urbain.—The following are the general results of the author's experimental work on cathode phosphorescence:—1. As Lecoq de Boisbaudran has maintained, pure substances exhibit no appreciable phosphorescence; bright phosphorescence is always due to the mixture of at least two substances. 2. In a phosphorescent binary system the optimum of phosphorescence always corresponds to small quantities of phosphorogen. 3. The optimum law is general, applying to ordinary substances and to the rare earths. 4. The coloration of the phosphorescence and its spectrum may vary with the degree of dilution of the phosphorogen. 5. With preparations made from pure substances all the spectral variations observed in the intermediate mixtures which the fractionation of the rare earths gives can be reproduced. Thus these variations do not prove that the fractionation has split a simple substance into several constituents. The optimum law may be enunciated as follows:—In every phosphorescent binary system in which the relative proportions of phosphorogen and diluent are varied each band of phosphorescence passes through an optimum, and the optima of different bands do not necessarily coincide, although they always correspond to relatively feeble proportions of phosphorogen.

Reduction of Uranyl Chloride.—Oechsner de Coninck.—Uranyl chloride is readily reduced at an incipient red heat by hydrogen, $\text{UO}_2\text{Cl}_2 + 2\text{H} = \text{UO}_2 + 2\text{HCl}$. This process the author has applied to determine the atomic weight of chlorine, but the results obtained did not agree very well; the mean value was 35.36. Uranyl chloride, moreover, has a tendency to dissociate into chlorine and a subchloride, and it reacts very readily with the water vapour of the air, giving hydrochloric acid and uranium trioxide, $\text{UO}_2\text{Cl}_2 + \text{H}_2\text{O} = \text{UO}_3 + 2\text{HCl}$.

Preparation of Ether Salts of the Cyclic Series.—A. Béhal.—When a mixture of benzyl chloride and acetic acid is heated, hydrochloric acid is set free and an ether salt of the cyclic radicle is formed. The author has shown that the hydrogen of the acid OH group is eliminated with the chlorine of the molecule of benzyl chloride, and benzyl acetate is thus formed. Many halogen salts of the metals or compounds of the metals which are decomposed by the hydric acids (oxides, carbonates, organic salts) promote the course of the reaction. Some of these substances induce condensation and some do not.

Preparation and Properties of β -Gluco-heptite.—L. H. Philippe.—By reducing β -gluco-heptonic lactone with sodium amalgam at -2° and eliminating the sodium sulphate formed by means of alcohol, a colourless syrup is obtained containing β -heptose and sodium heptonate. This syrup the author dissolved in water and treated again with sodium amalgam, shaking thoroughly. After separating the sodium sulphate and concentrating the solution the heptite may be isolated by dissolving in alcohol at 95° , in which sodium heptonate is insoluble. The composition of β -gluco-heptite corresponds to the formula $\text{C}_7\text{H}_{16}\text{O}_7$, the constitutional formula being—



It crystallises in little rectangular tablets which are hard and not hygroscopic. Its solubility in cold water is 50 per

cent and increases rapidly with the temperature. It is nearly insoluble in cold alcohol. It fuses at 130° to 131° like its α -isomer, but differs from the latter in optical activity, being feebly dextrorotatory in aqueous solution. It becomes laevo-rotatory in presence of borax.

Vol. cxlviii., No. 1, January 4, 1909.

Density of Methane. Atomic Weight of Carbon.—Georges Baume and F. Louis Perrot.—Accurate determinations of the density of methane show that the mean value of the weight of a normal litre is 0.7168 gm. From the molecular weight thus obtained the value of the atomic weight of carbon can be calculated. The mean value is found to be 12.004. Methane solidifies easily in liquid air. It fuses at -184° to a colourless mobile liquid, the density of which varies from 0.477 to 0.406.

Hydrogen Silicides.—P. Lebeau.—The author has treated a large quantity of magnesium silicide with hydrochloric acid and condensed the hydrogen silicides formed in liquid air. When the solidified products are allowed to assume the temperature of the air a gaseous product is obtained and a colourless liquid is left behind. By cooling the gaseous product in liquid air and slowly fractionating, Si_2H_6 is obtained and the liquid residue appears to be Si_2H_4 , which is very inflammable in oxygen.

MISCELLANEOUS.

Reduction of Salicylic Acid to Salicylic Aldehyde.—Hugo Weil.—Sodium salicylate is very readily reduced by sodium amalgam in aqueous solution at the ordinary temperature, if boric acid is also present, the product of the reaction being salicylic aldehyde. The yield is greater if an aromatic amine (especially *p*-toluidine) is added to the liquid. A difficultly soluble Schiff's base is thus formed, and up to 60 per cent of the theoretical yield of aldehyde can be obtained. The residue is a paste, probably a condensation product of salicylic alcohol.—*Ber.*, xli., No. 17.

MEETINGS FOR THE WEEK.

- TUESDAY, 9th.—Royal Institution, 3. "Architectural and Sculptural Antiquities of India," by Prof. A. A. Macdonell.
— Faraday Society, 8. "Applications of Electrolytic Chlorine to Sewage Purification and Deodorisation by the 'Oxychlorides' Process," by S. Rideal. "New Electrical Hardening Furnace," by E. Sabersky.
WEDNESDAY, 10th.—Royal Society of Arts, 8. "Bosnia and Herzegovina," by A. R. Colquhoun.
THURSDAY, 11th.—Royal Institution, 3. "Revival of Modern Drama," by William Archer, M.A.
FRIDAY, 12th.—Royal Institution, 9. "The Electrical Properties of Flame," by Prof. H. A. Wilson, F.R.S., &c.
— Physical, 8. (Annual General Meeting).
SATURDAY, 13th.—Royal Institution, 3. "Mendelssohn," Sir Alexander C. Mackenzie. (With the kind assistance of the Hans Wessely Quartette).

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DIAMONDS.

A Lecture delivered before the British Association at Kimberley.

By **SIR WILLIAM CROOKES**,
Hon. D.Sc. (Oxford, Dublin, and Cape of Good Hope), F.R.S.

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THE CHEMICAL NEWS.

Vol. XCIX., No. 2568.

THE ACTION OF PERMANGANATE ON FERROUS SALTS IN PRESENCE OF HYDROCHLORIC ACID.

By W. COLET BIRCH, B.A., A.I.C.

(Concluded from p. 63).

III.

THE gas evolved during the progress of some of the titrations resembled, as has been noted above, chlorine monoxide rather than chlorine.

In the event of the discrepancies being due to the irregular reaction of either of these two gases with ferrous salts, it was thought well to test their reaction under conditions similar to those which occur when a titration with permanganate is being carried out.

A solution of chlorine in water was prepared of such a strength that 22.51 cc. were equivalent in their iodine liberating power to 1 cc. of permanganate.

Twenty cc. of a ferrous solution were mixed with a little dilute sulphuric acid, 10 cc. of chlorine water were added, and the solution made up to 100 cc. For the completion of the oxidation 13.04 cc. permanganate were required.

The amount of permanganate for the complete oxidation of 20 cc. ferrous solution was 13.40 cc.

The actual difference found is 0.36 cc., that calculated is 0.44 cc.

In another titration in which 50 cc. of chlorine water were used, 11.22 cc. permanganate were required for completion of the oxidation.

The difference is 2.18 cc., and the calculated difference 2.22 cc.

Similar titrations were carried out with freshly prepared and standardised hypochlorous acid solution.

Twenty cc. of the ferrous solution, when mixed with 5 cc. hypochlorous acid, required 8.91, 8.89, 8.91 cc. permanganate; mean, 8.90 cc.

The amount of permanganate to oxidise 20 cc. ferrous solution was 12.20 cc.

The difference is 3.30 cc., and the calculated difference 3.39 cc.

The reaction therefore between ferrous sulphate and both chlorine and hypochlorous acid is regular.

If the discrepancies in the process are due merely to the liberation of chlorine, the amount of chlorine evolved should be equivalent in oxidising power to the excess of permanganate required in the first titration. To ascertain if such is the case, a titration was carried out in a closed flask through the cork of which the nozzle of the burette passed.

The permanganate required for 20 cc. of solution was 13.19 cc., the true value being 13.11 cc. The burette was replaced by a tube dipping into the liquid in the flask, and the flask attached to two U-tubes containing KI solution.

A current of air was aspirated through the apparatus for two hours, and the liberated iodine was titrated with thiosulphate; 2.67 cc. were required.

If all the available oxygen contained in the excess of permanganate had been used to oxidise the hydrochloric acid with the consequent liberation of iodine, 7.43 cc. of the thiosulphate solution would have been required instead of the 2.67 cc. found.

This points to the occurrence of another action besides that by which chlorine is liberated. This other action is probably responsible for the brown compound which is apt to obscure the end-point.

The brown solution obtained looks very like that pro-

duced when MnO_2 , Mn_2O_3 , or Mn_3O_4 is dissolved in concentrated hydrochloric acid and the solution kept cold. Pickering (*Journ. Chem. Soc.*, 1879, i., 654) showed that this solution contains $MnCl_3$, which, however, he did not isolate.

To investigate the reaction between HCl and $KMnO_4$ solution, both alone and when mixed with other salts, the following experiments were carried out:—

Mixtures of permanganate and hydrochloric acid were made, and air was then aspirated through the solution, the evolved gases being led into two U-tubes containing potassium iodide. The liberated iodine was titrated with thiosulphate solution.

Table VI. contains the results obtained. By comparing rows I., III., and IV. of Column 6 it is evident that $MgSO_4$ and Na_2SO_4 have no effect on the reaction, while in row II., in which $MnSO_4$ was present, there was an almost complete suppression of the chlorine.

In the case of row V. when ammonium sulphate was present the reaction seems to be quite anomalous, chlorine capable of liberating iodine, and also probably of oxidising ferrous salts, disappearing.

The addition of this salt before titrating would consequently be expected to have a distinctly bad effect. Such an effect is indeed noticeable, as will be seen on referring to Table IV.

Supposing that the brown solution contains the compound $MnCl_3$ investigated by Pickering, the reaction could be represented as follows:—



If this action takes place one-fifth of the total available chlorine would be left behind as $MnCl_3$, and four-fifths carried over into the potassium iodide.

The numbers in Column 7 of Series III. and IV should, if this view is correct, be one-fifth of the numbers in Column 6. In row III. this is approximately the case, while in row IV. multiplication by six gives a better result.

The agreement is perhaps as near as can be expected when the unstable nature of $MnCl_3$, and the possible existence of a less stable $MnCl_4$ (Nickles, *Ann. Chim. Phys.*, [4], v., 161), is taken into account.

IV.

Rice (*Journ. Chem. Soc.*, 1898) obtained crystalline double salts of KCl and NH_4Cl with $MnCl_3$ by adding saturated solutions of these salts to the cooled brown solution obtained by the action of hydrochloric acid on any of the higher oxides of manganese. It seemed advisable to try and obtain similar salts from the brown solution produced by the action of permanganate on hydrochloric acid. Dry hydrochloric acid was passed into a saturated solution of potassium permanganate and potassium chloride cooled in a freezing mixture of ice and salt.

Very little chlorine was evolved, the mixture turned deep brown, and at first a large quantity of potassium chloride was precipitated. This was separated, and the solution re-saturated with hydrochloric acid; a black precipitate was formed, which was filtered off, washed with concentrated hydrochloric acid, and dried in a calcium chloride dessicator containing some solid potash.

A black crystalline powder resulted which was decomposed by water, giving a copious precipitate of hydrated oxides of manganese and a smell of chlorine. It dissolved in strong hydrochloric acid, giving a deep reddish brown solution capable of liberating iodine from potassium iodide, and generally behaving in the same way as the brown solutions met with in the course of the above titrations.

The salt gave on analysis 16.09 per cent Mn, 25.78 per cent K, and 10.33 per cent Cl, capable of liberating iodine. The theoretical numbers for $MnCl_3 \cdot 2KCl \cdot H_2O$ are:—Mn, 16.74; K, 23.75; available Cl, 10.80.

The excess of potassium found is 2.03 per cent, and this calculated as KCl , probably present as impurity, is 3.87 per cent.

TABLE VI.

	1. HCl solution (293·9 grms. per litre).	2. KMnO ₄ solution (4·072 grms. per litre).	3. Salt added.	4. Water added.	5. Time for which air was passed. Hours.	6. Thio. for iodine liberated in U-tubes. Cc.	7. Thio. for iodine liberated on adding KI to solution in flask. Cc.	8. Sum of 6 and 7.	9. Thio. for iodine liberated by 10 cc. KMnO ₄ . Cc.
I.	Cc. 25	Cc. 10	—	Cc. 65	2	38·13	—	—	46·32
II.	25	10	25 cc. MnSO ₄ (150 grms. per litre)	40	2½	0·49	—	—	46·32
III.	25	10	25 cc. MgSO ₄ (246 grms. per litre)	40	2	38·14	7·80	45·94	46·32
IV.	25	10	25 cc. Na ₂ SO ₄ (142 grms. per litre)	40	2	38·85	6·13	44·98	46·32
V.	25	10	25 cc. (NH ₄) ₂ SO ₄ (132 grms. per litre)	40	2	2·14	1·16	3·30	46·32

On re-calculating the percentages, allowing for the presence of 3·87 per cent of KCl, there are obtained:—Mn, 16·74; and Cl, 10·74. The salt analysed was therefore the same as that obtained by Rice mixed with some potassium chloride.

Conclusions.

It seems obvious from the above that the brown solutions repeatedly met with are due to the presence of the compound MnCl₃. This accounts for the irregularities attendant on Marguerite's process when applied in presence of hydrochloric acid.

Since the brown colour is discharged on adding a ferrous salt, and since chlorine reacts regularly with the same, it is to be concluded that the irregular numbers of Table I. are due to the loss of a varying amount of chlorine from the solution, combined with the greater or less degree to which the action between HCl and permanganate has progressed.

The suppression of the chlorine evolution by the addition of excess of manganous salt is also explained, since Rice (*Journ. Chem. Soc.*, 1898) has shown that MnCl₂ and free chlorine when sealed up in a tube react slowly to give MnCl₃, and, further, Pickering (*Journ. Chem. Soc.*, 1879, xxxv., [1], 654) showed that the amount of manganic salt produced when MnO₂ dissolves in HCl is increased by the presence of MnCl₂, the increase being presumably due to the combination of the extra atom of chlorine with the MnCl₂ present.

This fact further explains the fair agreement of the numbers in Table V.

ERRATUM.—P. 61, Table, col. 8, line 3 from bottom, for "—0·09" read "+0·09."

King's College, Cambridge.

THE OSMOTIC PRESSURE OF CONCENTRATED SOLUTIONS, AND THE LAWS OF THE PERFECT SOLUTION.*

By GILBERT NEWTON LEWIS.

(Concluded from p. 64).

Note 1.

If a solution and the pure solvent are separated by a semipermeable membrane the solvent will flow through the membrane into the solution, where its escaping tendency is less. The only way of preventing this flow is to make the escaping tendency of the solvent the same on both sides of the membrane. There are two simple ways of accomplishing this, (1) to increase the pressure on the solution until the escaping tendency of the solvent in the solution is raised to equal that of the solvent in the pure state; (2) to diminish the pressure on the pure solvent

until its escaping tendency is lowered to equal that of the solvent in the solution.

The osmotic pressure may therefore be defined in two ways, (1) as usually defined it is the increase in the pressure on the solution necessary to bring the latter into equilibrium with the solvent; (2) Noyes (*Zeit. Phys. Chem.*, 1900, xxxv., 707), however, prefers to define the osmotic pressure as the diminution in the pressure on the solvent necessary to bring it into equilibrium with the solution. Neither of these definitions is entirely free from objections, but since the second one permits a much simpler mathematical treatment than the first, it has been adopted throughout this paper. The osmotic pressures defined in these two ways differ only when there is a total change of volume when a small quantity of solvent is added to a solution. There is no such volume change in the case of sugar and glucose as shown by the experiments of Morse and Frazer and of Ewan. We have been justified, therefore, in applying our equations, which involve the osmotic pressure according to the second definition, to the results of Morse and Frazer, who worked with the osmotic pressure of the first definition.

Note 2.

The exact equation connecting osmotic pressure and freezing-point may be found as follows:—Let us consider an aqueous solution in equilibrium with ice at the temperature T and the pressure p , and also in equilibrium with these, through a semipermeable membrane, pure water at the same temperature and at the pressure $p - \Pi$, Π obviously being the osmotic pressure. Now if the temperature changes by dT and the pressure on the solution and ice remains equal to P , that on the water must be changed in order to maintain equilibrium. The necessary change in pressure we will call $d\Pi$. Since the water and ice are in equilibrium at the beginning, the activity ξ of the water and the activity ξ' of the ice must be equal, and these, moreover, must remain constant as the temperature changes. Hence—

$$\xi = \xi'$$

and—

$$d\xi = d\xi'$$

or—

$$d \ln \xi = d \ln \xi'.$$

Now the change in the activity of the ice is due only to the change of temperature, that is—

$$d \ln \xi' = \left(\frac{\partial \ln \xi'}{\partial T} \right) dT,$$

but the activity of the water is changed both by the change in temperature and the change in pressure, that is—

$$d \ln \xi = \left(\frac{\partial \ln \xi}{\partial T} \right) dT + \left(\frac{\partial \ln \xi}{\partial \Pi} \right) d\Pi.$$

* From the *Journal of the American Chemical Society*, xxx., No. 5.

Equating the last members of these two equations, we have—

$$\left(\frac{\partial \ln \xi'}{\partial T}\right) dT - \left(\frac{\partial \ln \xi}{\partial T}\right) dT = \left(\frac{\partial \ln \xi}{\partial \Pi}\right) d\Pi.$$

Now, substituting for the partial differentials their values from the fundamental thermodynamic equations (Lewis, *loc. cit.*, Equations V. and VIII.; it is, of course, to be noted that, by definition, Π is a negative pressure), and combining the first two terms gives—

$$\frac{d\Pi}{dT} = \frac{-L}{vT};$$

where L is the heat absorbed in the fusion of 1 grm. of ice and v is the volume of 1 grm. of water. For T we may substitute $273.1 - \Delta$, where Δ is the lowering of the freezing-point below the centigrade zero, whence—

$$\frac{d\Pi}{d\Delta} = \frac{L}{v(273.1 - \Delta)}$$

In order to integrate this equation, L and v must be known as functions of Δ . According to a well-known principle the change of L with Δ is given by the equation—

$$L = L_0 - C\Delta;$$

where L_0 is the heat of fusion at 0°C . and C is the difference between the specific heats of water and ice. According to the best available data, C is about 0.5 if our unit of energy is the calorie, or 21 if our unit of energy is the cc.-atmos. The value of L_0 obtained in the very accurate experiments of Smith was 334.2 joules (*Phys. Rev.*, 1903, xvii., 231), assuming the electromotive force of the Clark cell to be 1.434 V at 15° . Since this value entered twice into the calculation of Smith, if we adopt for the Clark cell the value now accepted of 1.433 V, the value of L_0 must be lowered by 2 parts in 1434 and becomes 333.7 joules, or 3294 cc.-atmos. (Guttman, *Fourm. Phys. Chem.*, 1907, xi., 279, has made a similar re-calculation of Smith's value, but applied only one-half of the correction applied above).

We may therefore write—

$$L = 3294 - 21\Delta.$$

Strictly speaking, L is a function of the pressure also, but the pressure effect may easily be shown to be too small to be considered in the present calculation.

The volume of a grm. of water also depends upon both temperature and pressure. We shall see that 1 degree lowering of the freezing-point corresponds to about 12 atmos. change in the osmotic pressure. Hence from the known coefficients of thermal expansion and compressibility we find that the value of v may be expressed very closely by the linear equation,—

$$v = 1.000 + 0.0008 \Delta.$$

Substituting now in the above equation the values of L and v , and performing the multiplications and divisions indicated, we obtain $\frac{d\Pi}{d\Delta}$ as a series function of Δ , namely,—

$$\frac{d\Pi}{d\Delta} = 12.06 - 0.0414\Delta - 0.00009\Delta^2 + \dots$$

Except for very high values of Δ and Δ^2 term and all the higher terms are negligible. Dropping these terms, therefore, and integrating, we have—

$$\Pi = 12.06\Delta - 0.021\Delta^2.$$

By this equation the osmotic pressure corresponding to any freezing-point lowering may be calculated immediately, and, if the experimental data used are as accurate as they appear, the error of the calculation can hardly exceed a few tenths of a per cent even at osmotic pressures of several hundred atmospheres.

Note 3.

The connection between the osmotic pressure and the vapour pressure of the solvent from a given solution is obtained as follows;—From the fundamental thermo-

dynamic equation for the change of the activity of a substance with the pressure (Lewis, *loc. cit.*, Equation V.), we have—

$$\frac{d\ln}{d\Pi} = \frac{-V}{RT};$$

where V is the molecular volume and ξ is the activity of the pure solvent. When the vapour of the solvent behaves like a perfect gas whose pressure is p we may write—

$$d\ln \xi = d\ln p.$$

Hence, in such a case,—

$$\frac{d\ln p}{d\Pi} = \frac{-V}{RT}.$$

V may be regarded as constant for small values of Π but at high pressures we must consider the compressibility of the solvent. If the coefficient of compressibility of the solvent is denoted by α , and the volume when the osmotic pressure is zero by V_0 —

$$V = V_0 (1 - \alpha\Pi).$$

Substituting this value of V in the above equation and integrating, we have—

$$\Pi - \frac{\alpha}{2} \Pi^2 = \frac{RT}{V_0} \ln \frac{p_0}{p};$$

where p_0 is the vapour pressure of the pure solvent, p that of the solvent in the solution of osmotic pressure Π . This equation is derived for the case that the vapour of the solvent obeys Boyle's law. In any other case a more complicated formula must be used.

Summary.

The simple laws of the infinitely dilute solution become mutually incompatible in solutions of finite concentration. It is therefore necessary to choose one law to serve as a criterion of the perfect solution. The only law of dilute solutions which ever holds in concentrated solutions is the law of Raoult. This law is stated in a slightly modified form, and a perfect solution is defined as one which obeys this law. A number of solutions are mentioned which behave as perfect solutions over the whole range of concentrations, from 0 per cent to 100 per cent solute.

The indirect methods of determining osmotic pressure are discussed and an exact relation between the osmotic pressure and the freezing-point lowering of an aqueous solution is obtained. It is also pointed out that the osmotic pressure at one temperature may be obtained from that at any other when the heat of dilution is known.

Adopting Raoult's law in its modified form as the characteristic law of the perfect solution, it is possible with the aid of thermodynamics alone to obtain an equation connecting the osmotic pressure and concentration of a perfect solution. The equation thus obtained permits the exact calculation of osmotic pressures in perfect solutions, up to 1000 atmos. In comparatively dilute solutions the pressures thus obtained are substantially identical with those given by the equation of van't Hoff, as modified by Morse and Frazer, but at high concentrations the divergence between the two equations is very great.

An exact form is obtained for the mass law in concentrated perfect solutions.

Society of Public Analysts.—At the Annual General Meeting of the Society on February 3rd, the following Officers and Council were elected to serve during the year 1909:—President—R. R. Tatlock. Past-Presidents (limited by the Society's Articles of Association to eight in number)—M. A. Adams, Edward J. Bevan, Bernard Dyer, Thomas Fairley, W. W. Fisher, Otto Hehner, J. Augustus Voelcker. Vice-Presidents—Bertram Blount, Cecil H. Cribb, H. Droop Richmond. Hon. Treasurer—E. W. Voelcker. Hon. Secretaries—Alfred Chaston Chapman, P. A. Ellis Richards. Other Members of Council—W. J. A. Butterfield, H. C. H. Candy, Harold G. Colman, Arthur E. Ekins, John Golding, A. R. Ling, L. Myddelton Nash, James Nimmo, Frederic W. Richardson, F. G. Ruddock, G. E. Scott-Smith, Clarence A. Seyler.

SOME PROPERTIES OF THE RADIUM
EMANATION.

By E. RUTHERFORD, F.R.S.

IN 1906 (*Nature*, Oct. 25), I drew attention to the fact that the emanation of radium, thorium, and actinium were completely absorbed by cocoanut charcoal at ordinary temperatures. I have had occasion recently to repeat these experiments with much larger quantities of radium emanation, and have found that the actual volume of emanation capable of absorption by charcoal at room temperature is very small. For example, several grms. of cocoanut charcoal are required to absorb completely the emanation from 200 mgrms. of radium at ordinary temperature although the volume of the gas is only one-tenth of a cubic mm. As was to be expected, the absorptive power of charcoal for the emanation increases rapidly with lowering of the temperature. This was investigated as follows:—A quantity 0.8 gm. of cocoanut charcoal, which absorbed about 4 cc. of air at the temperature of liquid air, was connected with a pump, and the air completely removed by heating the charcoal. The charcoal was then surrounded by a pentane bath at $-150^{\circ}\text{C}.$, and the purified emanation from 83 mgrms. of radium (about 0.05 cubic mm.) absorbed in it. As the temperature of the bath slowly rose, the unabsorbed emanation was allowed to expand into an exhausted receiver of about 50 cc. capacity. This was pumped out at different temperatures of the charcoal, and the emanation collected and afterwards measured by the γ -ray method. At $-50^{\circ}\text{C}.$ the amount of unabsorbed emanation was less than one-tenth per cent of the total. Above $-40^{\circ}\text{C}.$ the emanation commenced to escape rapidly, and half had been pumped off at a temperature of $10^{\circ}\text{C}.$ About 19 per cent remained in the charcoal at $100^{\circ}\text{C}.$, but practically all was released at a temperature of the softening of glass. It is seen from these results, that at $10^{\circ}\text{C}.$ the charcoal absorbs about 0.03 cubic mm. of emanation per gm., and at $-40^{\circ}\text{C}.$ about 0.06 cubic mm. per gm.

An experiment was shown to illustrate the rapidity of condensation of pure emanation contained in an exhausted vessel when one point was cooled to the temperature of liquid air.—*Memoirs and Proceedings of the Manchester Literary and Philosophical Society*, vol. liii., Part I.

FURTHER INVESTIGATION OF THE
ATOMIC WEIGHTS OF NITROGEN AND SILVER.*By THEODORE WILLIAM RICHARDS, PAUL KÖTHNER,
and ERICH TIEDE.

(Concluded from p. 66).

Analysis of the Ammonium Chloride.—In the present research the amount of chlorine present was determined by precipitating the halogen as silver chloride and weighing this substance. A further check upon the method, obtained by finding the silver necessary for precipitation, was not completed for lack of time, but this further step is now being taken in the Chemical Laboratory of Harvard College. The method of analysis is so similar to that used in the case of sodium and potassium chlorides that few words need be spent upon the description (*Publications* Nos. 28 and 69 Carnegie Inst. of Washington). In the first place exactly the equivalent amount of silver was added to effect the precipitation, and then after much shaking and long standing, a slight excess of about 0.05 gm. per litre of silver nitrate was added. Filtration was effected by means of the Gooch-Munroe-Neubauer crucible with the help of the water-pump. The first two washings were made with water containing a trace of silver nitrate, then three further washings with about 0.2 litre of pure

water each were used, and then 3 to 5 washings with small volumes of water containing nitric acid. Afterwards the precipitate was conveyed with the greatest care by means of a jet of water driven by hydrostatic pressure into the crucible, and finally the flask was rinsed with ammonia, and the solution tested in the nephelometer in order to be sure that every trace of silver chloride had been collected. The further drying and fusing of the silver chloride happened precisely in the usual way, and the product was as pure and white in appearance as could have been desired. Concentrated ammonia was used to remove traces of silver chloride from the perforated crucible in order to prepare it for further work.

The determination of the silver chloride dissolved by the wash waters, one of the most important parts of the whole proceeding, occurred in the usual way with a nephelometer, proceeding as has already been described by Richards and Staehler. The weighing was conducted entirely by methods of substitution as usual, and all the weights were corrected to the vacuum standard. In view of the fact that the details are essentially like the previous work of the kind, further particulars are unnecessary, and the final table of results may be given at once. This table contains only those analyses which were believed to be free from error. Two preliminary determinations, vitiated by inexperience, were rejected. Four other experiments also, Nos. 5, 6, 8, and 10, were likewise rejected, because of the small amount of material used, averaging less than a gm. in these cases. One of these four, No. 6, was known to be in error for other reasons. The three of these which might possibly have been included, namely, Nos. 5, 8, and 10, would have made very little difference in the final result, but it was thought safer to exclude them, because the method is too complicated to yield satisfactory results with so small a quantity of substance.

RATIO OF ARGENTIC TO AMMONIC CHLORIDE
(FINAL RESULTS).

Ag = 107.881; Cl = 35.4574; H = 1.0076.

No.	Sample.	NH ₄ Cl (in vacuo).	AgCl (in vacuo).	AgCl:NH ₄ Cl = 100 : x.	Atomic weight of nitrogen. Ag = 107.881. Cl = 35.4574. H = 1.0076. N =
		Grms.	Grms.	x =	
3.	C	2.02087	5.41469	37.3220	14.009
4.	A'	2.23894	5.99903	37.3217	14.008
7.	B	1.55284	4.16076	37.3211	14.008
9.	A	1.36579	3.65959	37.3209	14.007
11.	B	1.61939	4.33914	37.3205	14.007
12.	D	1.93795	5.19219	37.3243	14.012
13.	D	2.89057	7.74498	37.3219	14.009
14.	B	1.31405	3.52082	37.3223	14.009
15.	B	1.82091	4.87921	37.3198	14.006

Average 37.3217 14.0085
Probable error ± 0.0004

(The analyses tabulated in this list were all made in Berlin by E. Tiede, with the immediate collaboration of P. Köthner, after T. W. Richards had been obliged by his duties in Harvard University to return to America).

Discussion of the Results.—From these figures it is clear that the atomic weight of nitrogen cannot be far from 14.008 if silver is taken as 107.88. The results agree with one another as well as could reasonably be expected. The maximum deviation from the mean is 4 in the third decimal place, and in no other case does the deviation exceed 2. The average deviation from the mean is only about 1 in the third decimal place, and the probable error calculated according to the theory of least squares is ± 0.0004 . This probable error of course gives no clue to any constant error which may possibly have escaped detection, but its small value shows at least that further repetition of the process by this method is not necessary.

* *Journal of the American Chemical Society*, xxxi., No. 1.

It is interesting to compare the results from the four different samples of ammonium chloride. Sample A and A' were made from ammonia prepared from ammonium sulphate oxidised by nitric acid, and by sulphuric acid with permanganate. The preparation of the salt occurred in the case of A in quartz dishes, in A' in platinum dishes. The results of these two are essentially identical, giving an average of 14.0075. Sample B was made from ammonia prepared by the electrolytic reduction of nitric acid, neutralised with pure hydrochloric acid in quartz vessels alone. The four analyses of this substance gave exactly the same result, on the average, 14.0075. Samples C and D, which were made, the one in Germany and the other in America, by the action of nitric acid on ammonium chloride gave a slightly higher value, the average of the three being 14.010. It is probable that the method of preparation in these cases was not so effectual as in the others; small quantities of carbon compounds may have still remained in the material. The number of analyses is, however, too small to make certain of this difference, which is at worst very slight; and accordingly the results may be averaged in with the others without causing serious error.

The relation of these results to other atomic weights is very far-reaching and important. Clearly, they connect the atomic weight of nitrogen with that of hydrogen, silver, and chlorine, and therefore with the help of other well-known relations affect the atomic weight of each of these elements in relation to the other. The calculation is very simply carried out as follows:—

Let—

$$\frac{\text{AgCl}}{\text{Ag}} = a \dots\dots\dots 1,$$

$$\frac{\text{NH}_4\text{Cl}}{\text{AgCl}} = b \dots\dots\dots 2,$$

$$\frac{\text{AgNO}_3}{\text{Ag}} = c \dots\dots\dots 3.$$

The three atomic weights supposed to be unknown may be designated as follows:— $\text{Ag} = x$, $\text{Cl} = y$, $\text{N} = z$. From the work of Morley hydrogen may be taken as 1.0076, if oxygen = 16 (*Am. Chem. Journ.*, xvii., 267; *Zeit. Phys. Chem.*, 1895, xvii., 87). Substituting these values in Equations 1, 2, and 3, we obtain the following:—

$$x + y = ax \dots\dots\dots 4,$$

$$z + y + 4.034 = b(x + y) \dots\dots\dots 5,$$

$$x + z + 48.000 = cx \dots\dots\dots 6.$$

Substituting in Equation 5 the value of z as found from Equation 6, we have—

$$(1 - c)x - bx + (1 - b)y = 43.9696,$$

but according to Equation 4 $y = (a - 1)x$; hence—

$$x = \frac{43.9696}{1 - c - b + (1 - b)(a - 1)}$$

The values a , b , and c are all known. a (the quantity of silver chloride obtained from 1 grm. of silver) was found by Richards and Wells to be 1.32867 (*Publication No. 28 Carnegie Inst.*; *Journ. Am. Chem. Soc.*, xxvii., 526); c (the quantity of silver nitrate obtained from the same quantity of silver) was found by Richards and Forbes to be 1.57479 (*Publication No. 69 Carnegie Inst.*; *Journ. Am. Chem. Soc.*, xxix., 826). The present investigation gives the value of b as 0.373217, the average of the fifth column in the preceding table. Substituting these values in the Equation 7, we obtain x , the atomic weight of silver, = 107.881. Substituting this value in Equation 4, we obtain y , the atomic weight of chlorine, = 35.4574, and substituting these values in Equation 5 or 6, we obtain z , the atomic weight of nitrogen, = 14.0085. These three values for the atomic weights of silver, chlorine, and nitrogen are entirely independent of any but the most recent work, and rest directly, through silver nitrate

and water, upon the international standard of atomic weights, $\text{O} = 16.000$. It may be noted that if hydrogen is taken as 1.0078 with Noyes (*Journ. Am. Chem. Soc.*, 1908, xxx., 4), the values of the atomic weights are altered but slightly. Silver becomes 107.879, chlorine 35.456, nitrogen 14.008. The present work thus completes a connected chain of data, and furnishes striking evidence in favour of the low values for silver and nitrogen which have recently found support in so many other different ways.

It is not without interest also to note that if one chooses the value for silver, 107.93, and for chlorine, 35.473, the present work makes nitrogen 14.017—a value inconsistent with the value 14.037 calculated from silver nitrate, if silver is assumed as 107.93. Thus the present results are incompatible with the work of Stas, both as regards silver and as regards nitrogen.

Summary.

In the present paper is described a series of analyses of ammonium chloride. These analyses were superior to any other that have ever been made in respect, first, to the purity of the material; second to the choice of conditions for subliming the salt; and third, to the accuracy of the analyses. The ammonium salt was prepared in such a way as to render the presence of amines very unlikely; the sublimation was conducted first in a current of ammonia, and then the same substance was re-sublimed in a vacuum; the analysis was carried out with all the care used in the recent work in Harvard University, taking due account of the solubility of silver chloride. As a result, it was found that if oxygen is taken as 16.000 and hydrogen as 1.0076, the three following values result:— $\text{Ag} = 107.881$, $\text{Cl} = 35.457$, and $\text{N} = 14.008$.

TANTALUM AND NIOBIUM IN AUSTRALIA.

By EDWARD S. SIMPSON, B.E., F.C.S.,
of the Geological Survey of Western Australia.

(Concluded from p. 52.)

THE mineral which occurs most frequently at Wodgina, and constitutes almost the whole bulk of the ore exported, is manganotantalite. A typical fragment from a large specimen of detrital ore from miscellaneous lease 86 was analysed with the results given in Column A. Those in Column B were obtained from a single rhombic prism weighing 8 grms.

	A.	B.
Tantalum pentoxide	68.65	69.95
Niobium pentoxide	15.11	14.47
Titanium dioxide	0.40	—
Tin dioxide	0.48	0.36
Tungsten trioxide	Trace	—
Water combined	0.07	—
Iron protoxide	1.63	2.68
Manganese protoxide	14.15	(12.54)
Nickel protoxide	Trace	—
Lime	Trace	—
Magnesia	0.15	—
Cerium and yttrium oxides	Nil	Nil
Total	100.64	100.00
Specific gravity	7.03	7.09

This mineral is black on a fresh fracture with a metallic lustre. Weathered surfaces are a rusty-brown colour, due largely to a thin adhering film of ferruginous clay. The masses, whether of lode or detrital ore, frequently consist of an intergrown mass of parallel prismatic crystals, in which the faces a , b , and c are freely represented, and, less commonly, u (133). These prismatic masses are inclined at times to be wedge-shaped, and, rarely, small masses are seen to be part of a spherical "rosette" or radiated crystal group. The faces are frequently indented by actual tabular crystals of albite, or by hollows from which albite

has evidently been weathered out. Twinning about the plane *e* has been observed in several instances. The macropinacoid *a* is often vertically striated, and at times has a very brilliant lustre. In size the masses vary from many pounds in weight down to a few grains only, and in the alluvial are often associated with tin ore, though so far cassiterite has not been recorded from the veins which carry tantalite.

No normal iron tantalite has been observed at Wodgina, the whole of the tantalite there being of the manganese variety. It is usually of very uniform grade, containing from 65 per cent to 70 per cent of tantic oxide. Manganocolumbite has, however, recently been obtained at Wodgina. This is identical with the richer ore, in all physical features, with the exception of specific gravity, which, as one would expect, is correspondingly lower. Specimens of this mineral, and of an ore of intermediate composition, gave the following results.

	Tantic oxide.	Niobic oxide	Sp. gr.
Manganocolumbite	22.90	54.83	5.72
Low-grade manganotantalite	48.21	30.52	6.34

In "Dana's Mineralogy" there is a list of analyses of tantalite-columbite from the Etta Mine in the Black Hills of South Dakota, which show to what a large extent the ore in a single mine may vary in grade owing to the mutual replacement of tantalum by niobium, and *vice versa*. As has already been stated, this is not characteristic of most of the Wodgina deposits. The exception that proves the rule, however, is a small parcel of crystalline stream ore, individual fragments of which gave the following specific gravities:—5.98, 6.10, 6.55, 6.92, 7.03, 7.75, 8.03. These figures show that this ore ranges from nearly pure niobate of manganese to a nearly pure tantalate of iron.

Tin oxide appears to exist as an essential constituent of all tantalates and niobates. The amount thus present seldom exceeds 1 per cent, and, not being recoverable by any simple process, is of no importance to the miner. A mechanical mixture, however, of cassiterite and tantalite or columbite is readily separated by an electro-magnet, so that the cassiterite which thus occurs with almost all Wodgina stream ores is not to be overlooked. The following figures give an idea as to the extent to which the tin thus occurs:—

Sample.	Tantic oxide. Per cent.	Niobic oxide. Per cent.	Metallic tin. Per cent.
A	45	32	3.12
B	60	16	6.74
C	17.3	3.5	50.35
D	8.9	1.6	60.90

Microlite (pyrotantalate of lime) occurs in association with manganotantalite in a stream ore received from Wodgina. The exact locality from which this ore was derived has so far not been disclosed, but, judging from the associated minerals, it is from the immediate vicinity of Wodgina itself. The mineral, constituting about 2 per cent of the whole parcel, is in irregular water-worn fragments up to 1 in. in diameter. By the courtesy of Mr. A. O. Watkins I have been supplied recently with about an ounce in weight of this mineral, and a preliminary physical and chemical examination of it has been made.

The specific gravity of five fragments was respectively 5.37, 5.76, 5.61, 5.42, 5.73, evidencing a somewhat small variation in tantalum contents (probably about 15 per cent). No evidence of crystallisation is apparent, the fragments being roughly rounded and water-worn. Parts of the surface are covered with a very thin black coating, which sends out what one may call small rootlets into the mass of the mineral. This coating, as well as more or less numerous minute black inclusions in the centre of the pebbles, appears to consist of tantalate of manganese. Where not covered with this black coat the microlite pebbles are grey or light pinkish brown. On fresh fractures the mineral is opaque and usually light pinkish grey, sometimes a little darker, and inclined to liver-colour. The

internal structure as seen in a thin slice under a microscope is very interesting, being reminiscent of olivine largely altered to serpentine. It consists of numerous cores of clear unaltered isotropic microlite enclosed in a mesh-work of the same mineral, more or less cloudy, and evidently altered somewhat—probably, judging from the analysis, by absorption of water. Throughout the section are tiny pin-points of black manganotantalite.

A fragment of a pale pinkish colour, which on sectioning was found to be practically free from included tantalite, was chosen for analysis. It has, unfortunately, not been found possible so far to complete this analysis, but the following are the results obtained up to the present:—

Tantalum pentoxide	}	77.16
Niobium pentoxide		
Lime		13.46
Magnesia		0.42
Iron protoxide		3.64
Manganese protoxide		0.60
Potash		0.20
Soda		1.66
Water on ignition		1.06
Water at 100°		0.22

98.42
Specific gravity 5.422

The analysis proves this mineral to be essentially a pyrotantalate of lime of the form $\text{Ca}_2\text{Ta}_2\text{O}_7$, part of the lime being replaced by alkalis, iron oxide, &c. Like most tantalum minerals, it probably carries a little tin oxide, which has not been estimated.

Of interest in this connection are a few small pebbles received on another occasion from Wodgina. One consists of a large core of a dark coloured tantalate, completely surrounding which is a layer about 5 millimetres thick of pale microlite similar to that described above, covered in its turn again by a very thin coating of black tantalite. A second pebble is similar, whilst two others are wholly composed of a greyish black opaque and apparently homogeneous mineral. One of these latter pebbles, weighing 18 grms., was broken in half, and one half analysed with the following result:—

Tantalum pentoxide	73.82
Niobium pentoxide	6.44
Tin dioxide	0.72
Titanium dioxide	0.54
Iron protoxide	8.42
Manganese protoxide	1.39
Lime	7.78
Magnesia	0.62
Cerium and yttrium oxides	Nil

99.73
Specific gravity 6.04

Without further investigation it is impossible to say whether this is only a very intimate intergrowth of microlite and tantalite, or, as I am inclined to think, a new sub-species of tantalite, in which lime to a large extent replaces iron oxide. If the latter be the true explanation of the observed facts, the name calciotantalite naturally suggests itself as descriptive.

Mount Francisco.—This locality is about 15 miles south-west of Wodgina, and has only recently been discovered. According to accounts of the field received in Perth, the ore occurs under similar conditions to those which obtain at Wodgina. The mineral, however, contains much less tantalum, being a manganocolumbite with specific gravity 5.73, equal to 23 per cent of tantic oxide. The pegmatite in which the ore occurs is composed mainly of albite, orthoclase, and quartz, with more or less muscovite and garnet. The columbite is in irregular masses, in which parallel groups of crystals are often well defined. The faces most commonly developed are *a* (striated), *b*, and *u*. Twinning on *e* was observed in one case. Small parallel

crystals are developed in great numbers at times on the macropinacoid *a*.

A little detrital ore has been obtained from this locality. It is thickly coated with ferruginous clay, which is sufficiently adherent to give a rusty-black colour to the ore, even after hard scrubbing with water. The actual ore itself does not apparently weather readily, as careful cleaning reveals bright black faces. The ore has not travelled far, as excellent crystals with sharp edges occur amongst it.

Greenbushes.—The last locality to be described was almost the first in which tantalum and niobium were recognised in Australia. It is interesting also as being the scene of the first mining for tantalum or in the Commonwealth, a lease having been secured and worked in 1902 to provide tantalite for the Foote Mineral Company of the United States.

Greenbushes is situated in the Blackwood Ranges. The prevailing rock on the surface is a laterite composed largely of bauxite, and completely concealing the underlying primary rocks from view except in a few isolated areas adjacent to streams. The country appears to be mainly granite, traversed by dykes of diorite and pegmatite, all foliated more or less strongly in places. Considerable quantities of tin ore have been recovered from the streams and older gravels and cements, smaller quantities from the pegmatite dykes and foliated bands of greisen.

In 1893 Mr. J. J. East, of the Adelaide School of Mines, in examining some alluvial tin ore from Greenbushes, turned his attention to a mineral present in it, which had been looked upon by the miners as "resin tin," or in some cases as scheelite. A few blowpipe tests revealed the fact that this mineral was a new compound of antimony. It was therefore submitted for analysis to Mr. G. A. Goyder, who established the fact that it was a tantalate and niobate of antimony. This new mineral species was subsequently named stibiotantalite.

Although only present in the ores from the southern part of the field, and even then in quantities not exceeding 1 per cent or 2 per cent, stibiotantalite threatened at one time to become a serious trouble to the tin miners, as the antimony from it found its way into all the smelted tin, and reduced its value by about £10 per ton. It would appear to have almost disappeared from the ores raised in recent years, only occasional very small fragments being seen in the concentrates.

In 1900, at the time when the author was examining some of the antimonial tin ores with a view to suggesting a method of treatment, trouble was again experienced at Greenbushes with a second class of concentrates. Some apparently clean tin concentrates from alluvial ground refused to yield up any tin either in the assay pot or in the smelting furnace. Several samples of this mysterious ore were forwarded to the author, and proved to be tantalite of the normal iron variety. No other tantalum minerals have so far been detected at Greenbushes, except a doubtful new species, a hydrated tantalate of antimony, which will be described later.

Very little lode mining has been done at Greenbushes, either for tin or tantalum; the total tantalum ore exported—2½ tons—having been obtained almost exclusively from alluvial workings. The principal lode workings are at the head of Bunbury Gully, on mining lease 369 (Enterprise), where there is an ore body 18 inches wide, consisting of a crushed rock composed almost wholly of pale-green mica with accessory quartz, tourmaline, cassiterite, and tantalite in fragments from the size of sand up to an inch in diameter. Overlying the lode is 12 feet of alluvial, carrying fine and coarse tinstone and tantalite.

On mining lease 379 (Galtee More), one mile further south, a decomposed lode of apparently similar character carries tin and tantalite. Some lode tin concentrates from mining lease 56 (Amanda), lying between these two, was found to yield on assay 5·5 per cent of mixed tantalic and niobic oxides. This ore is described as coming from a weathered tourmaline bearing dyke.

The alluvial tantalite at Greenbushes occurs principally in Bunbury and Floyd's gullies, in fragments from the size of sand grains up to lumps 13 lbs. in weight. Its composition is not very variable, and, as shown by the following analysis of a typical fragment, it is a high-grade ore, occurring, unfortunately, in very limited quantities.

Tantalum pentoxide	80·61
Niobium pentoxide	2·50
Tin dioxide	1·51
Titanium dioxide	0·71
Tungsten trioxide	0·13
Water combined	0·14
Iron protoxide	10·89
Manganese protoxide	3·78
Nickel protoxide	0·02
Lime	Nil
Magnesia	0·19
Cerium and yttrium oxides	Nil

Specific gravity 100·48
7·74

This specimen, like all others from Greenbushes, showed no traces of crystal faces but exhibits an ill-defined cleavage. Dr. G. F. Kunz reports that its radio-activity is less than 0·02 times that of uranium. The mineral is of a brownish-black colour, and on a fresh fracture has a bright metallic lustre. Some fragments are wholly or partially coated with a smooth, hard, and strongly adherent coating of ferruginous bauxite, as much as 3 or 4 millimetres thick in places. This peculiarity extends to the tin ore also. Other fragments have no decided coating, but a slightly rusty tinge, which enables them to be readily picked out from the associated tin ore. Quartz, weathered felspar, and stibio-tantalite are found adherent to it, whilst associated with it in the gravels are cassiterite, tourmaline, quartz, mica, cyanite, and other minerals.

The most interesting mineral found at Greenbushes is the previously mentioned stibiotantalite. This has not yet been located in lode material; but in some parts of the southern part of the field was at one time somewhat plentiful in the stream deposits. It was never shown to exist in amounts which would justify its being put on the market as a tantalum ore, and as time goes on it appears to become more and more rare. Greenbushes was, up till recently, the only known locality for this mineral, but quite recently well-defined orthorhombic crystals have been found at Mesa Grande, California, in a pegmatite vein, with tourmaline, beryl, &c.

The chemical composition of the Greenbushes mineral is shown by the following two analyses by Mr. G. A. Goyder:—

	A.	B.
Tantalum pentoxide	51·13	51·95
Niobium pentoxide	7·56	4·49
Silica	—	3·14
Combined water	—	0·61
Antimony trioxide	40·23	38·04
Bismuth trioxide	0·82	0·79
Iron peroxide	Trace	0·39
Manganese protoxide	—	Trace
Nickel protoxide	0·8	Trace
Copper oxide	—	0·20
	99·82	99·61

Specific gravity 7·37 6·47

Its formula is $\text{Sb}(\text{TaNb})\text{O}_4$, or more probably, according to Penfield and Ford, $(\text{SbO})_2(\text{TaNb})_2\text{O}_6$, which would explain the resemblance of its crystals to those of columbite.

Two well-marked features of the Greenbushes ore are of great interest, as indicating the probable origin of the mineral. In the first place stibiotantalite is often seen filling minute veins and occupying small vughs in masses of tantalite. Secondly, a very large number of the water-worn pebbles contain a central core of tantalite, the boundaries of which are very irregular, and which pene-

trates often in thin tongues out into the surrounding stibiotantalite. It would appear that the original mineral has been tantalite, and that this has been more or less replaced by pseudomorphs of stibiotantalite on the infiltration at a later stage of antimonial solutions into the lodes.

Greenbushes stibiotantalite exhibits only occasional traces of an external crystalline form: the only faces recognised with any certainty are *a* and *b*, with possibly *m* and *u*. A very distinct cleavage parallel to the macro-pinacoid is almost invariably noticed, and at times traces of a second cleavage have been seen. In colour and transparency it varies very largely. Many small fragments are perfectly transparent, and of a pale lemon-yellow or amber colour; the greater part of the ore is, however, more or less opaque, and varies in colour from light yellow or grey to brown or even dull black. Some of the more opaque mineral is cellular in structure, shows no cleavage, has a dull rough surface, and breaks with an uneven fracture. This may be an alteration product of true stibiotantalite, one such specimen yielding an amount of water of combination expressed by the formula $(\text{SbO})_2\text{Ta}_2\text{O}_6\cdot 7\text{H}_2\text{O}$. Such a fragment had a specific gravity of only 4.77. In the unaltered stibiotantalite Goyder found a range in specific gravity from 6.47 to 7.37. The author has made the following specific gravity determinations, amongst others:—6.41, dark yellow pebble; 6.75, grey pebble; 7.18, grey pebble, with yellow veins, strong cleavage; 7.43, pale lemon-yellow, indistinct crystal; 7.48, dark yellow crystalline; 7.50, pale greyish yellow, indistinct crystal. The bulk sample from which most of these pieces were taken assayed tantic oxide, 50.57 per cent; niobic oxide, 12.58 per cent. A second bulk sample assayed tantic oxide, 51.13 per cent; niobic oxide, 7.56 per cent.

The stibiotantalite occurs in fragments from the size of a pin's head up to about 1 inch in diameter. A single exceptionally large crystalline mass, about 2½ inches in diameter, is in the possession of the Foote Mineral Company.

This mineral has been examined for radio-activity, with negative results, by Messrs. Mawson and Laby.

Conclusion.

In conclusion I desire to express my indebtedness to several gentlemen for the material information obtained from their letters or published papers. Amongst others, I am specially indebted to Messrs. A. Gibb Maitland, C. W. Marsh, G. A. Goyder, D. Mawson, and J. C. H. Mingaye.

PROCEEDINGS OF SOCIETIES

CHEMICAL SOCIETY.

Ordinary Meeting, January 21st, 1909.

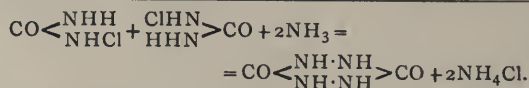
Sir WILLIAM RAMSAY, K.C.B., F.R.S., President,
in the Chair.

(Concluded from p. 70).

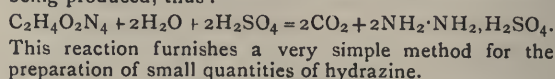
*4. "Synthesis of Para-urazine from Carbamide." By FREDERICK DANIEL CHATTAWAY.

By means of dichlorocarbamide, $\text{NHCl}\cdot\text{CO}\cdot\text{NHCl}$, recently described by the author (*Proc. Roy. Soc.*, 1908, lxxxi., A, 381), carbamide can be very simply converted into *p*-urazine, which has hitherto only been obtained by the employment of hydrazine. All that is necessary is to add an aqueous solution of dichlorocarbamide to a strong solution of ammonia, when *p*-urazine, which is very sparingly soluble in water, separates as a white, crystalline precipitate.

In the reaction, one of the chlorine atoms of the dichlorocarbamide is probably replaced by hydrogen, two molecules of the resulting monochlorocarbamide then condensing under the influence of the ammonia, thus:—



p-Urazine is readily hydrolysed when heated with concentrated sulphuric acid, carbon dioxide and hydrazine sulphate being produced, thus:—



DISCUSSION.

Dr. HEWITT called attention to the analogy between Dr. Chattaway's process for obtaining hydrazine and the method devised by Raschig, namely, the direct action of hypochlorites on ammonia.

*5. "Chlorine Derivatives of Substituted Carbamides." By FREDERICK DANIEL CHATTAWAY and DONALD FREDERICK SANDYS WÜNSCH.

The action of chlorine on carbamide should give rise to a monochloro-, a symmetrical and an unsymmetrical dichloro-, a trichloro-, and a tetrachloro-carbamide. Of these, only the *s*-dichloro-derivative has so far been isolated. The action of chlorine on a number of substituted carbamides has been studied, and it has been shown that in such compounds it is possible to replace by chlorine all the hydrogen attached to nitrogen, atom by atom.

Compounds of the types $\text{NHR}\cdot\text{CO}\cdot\text{NHCl}$, $\text{NCIR}\cdot\text{CO}\cdot\text{NHCl}$, $\text{NCIR}\cdot\text{CO}\cdot\text{NCl}_2$, $\text{NCIR}\cdot\text{CO}\cdot\text{NCIR}$, and $\text{NR}_2\cdot\text{CO}\cdot\text{NCl}_2$ have been obtained, R being an acyl or an alkyl group.

The monochloroacylcarbamides are beautifully crystalline solids, which are among the most stable of the nitrogen chlorides known. The acyl compounds containing more chlorine, and most of those containing an alkyl group, are liquids which decompose easily on heating.

Nearly all of the possible chlorine derivatives of acetyl-, benzoyl-, methyl-, *s*- and *as*-dimethyl, ethyl, *s*-diethyl-, and benzyl-carbamide have been prepared.

It is thus proved that in carbamides the replacement of one hydrogen atom by chlorine does not prevent in any way the replacement of the second hydrogen atom attached to the same nitrogen.

There is every reason, therefore, to believe that the action of chlorine on carbamide itself gives rise to the other theoretically possible chlorocarbamides, and that these will be obtained when the conditions under which they can exist are ascertained, and when the difficulties attending their isolation have been overcome.

*6. "Chemical Examination of Eriodictyon." Part II. By FRANK TUTIN and HUBERT WILLIAM BENTLEY CLEWER.

Eriodictyon leaves were shown by Power and Tutin (*Proc. Am. Pharm. Assoc.*, 1906, liv., 352) to contain, in addition to other compounds, three new crystalline substances of a phenolic nature, namely, eriodictyol, $\text{C}_{15}\text{H}_{12}\text{O}_6$ (m. p. 267°), homoeriodictyol, $\text{C}_{16}\text{H}_{14}\text{O}_6$ (m. p. 223°), and a third substance, possessing the formula $\text{C}_{16}\text{H}_{12}\text{O}_6$, which occurred only in very small amount.

The present authors have employed a larger amount of the extract of *eriodictyon* leaves, and, after a prolonged process of separation, have isolated a larger amount of the last-mentioned compound, together with two new substances.

Chrysoeriol, $\text{C}_{16}\text{H}_{12}\text{O}_6$, the substance previously isolated in small amount, forms golden-yellow leaflets, and does not melt at 337°. It contains three hydroxyl groups, and yields *triacetylchrysoeriol*, $\text{C}_{16}\text{H}_9\text{O}_6(\text{CO}\cdot\text{CH}_3)_3$, which melts at 211–212°.

Xanthoeridol, $\text{C}_{18}\text{H}_{14}\text{O}_7$, crystallises in yellow needles melting at 258°. *Triacetyl-xanthoeridol*, $\text{C}_{18}\text{H}_{11}\text{O}_7(\text{CO}\cdot\text{CH}_3)_3$, melts at 175–176°.

Eriodonol, $\text{C}_{19}\text{H}_{18}\text{O}_7$, separates from dilute alcohol in pale yellow needles, which contain one molecule of water

of crystallisation and melt at 199° ; the anhydrous substance melts at 209° . It yields a *tetra-acetyl* derivative melting at 131° .

"7. *The Hydration of Precipitates.*" By SPENCER U. PICKERING.

Many substances which are precipitated from aqueous solution are capable of emulsifying oils, and, by adjusting the amount of oil in the emulsion, the latter may be obtained of the same density as the liquid. By determining the density of this liquid, the density of the oil, and that of the precipitate in the anhydrous conditions, and by ascertaining the weight of oil required to float a given weight of precipitate in two liquids of different densities, the weight of water combined with the anhydrous precipitate may be determined. The precipitate selected was the compound $10\text{CuO}\cdot\text{SO}_3\cdot\text{CaSO}_4\cdot\text{Na}_2\text{SO}_4$, which is of uniform composition when thrown down by adding lime-water to copper sulphate in the presence of varying quantities of sodium sulphate. The amount of water combined with it was found to be about $42\text{H}_2\text{O}$. It was also ascertained that the water possessed the same specific gravity of ice, as in the case of the water of crystallisation of most hydrated salts.

DISCUSSION.

The PRESIDENT called attention to the fact that Dr. Chichester Bell had, more than ten years ago, made experiments on the velocity of sound in melted ice at $+0.5^{\circ}$, and in cooled water at the same temperature. The velocities appeared to differ. Experiments by Dr. Wilmore, unpublished, on the density of melted ice, and of cooled water, were indecisive, owing to the lapse of time before an accurate density could be determined.

He also reminded Mr. Pickering that Playfair and Joule had concluded from their experiments that "water of crystallisation" has the same molecular volume as ice.

"8. *Studies of Dynamic Isomerism.* Part VIII. *The Relationship between Absorption Spectra and Isomeric Change. Absorption Spectra of Halogen, Nitro-, and Methyl Derivatives of Camphor.*" By THOMAS MARTIN LOWRY and CECIL HENRY DESCH.

The band noted by Baly and by Hartley in the ultra-violet absorption spectrum of camphor at a concentration of N/10 appears also in the spectrum of β -bromocamphor; in both cases the band is weakened by diluting to N/100, but is restored by the addition of alkali. A similar band of rather greater intensity is seen in the spectrum of α -bromocamphor at a concentration of N/100; as this band is developed by neutral solutions in which the α -bromo-compound is stable, and is only slightly intensified when a condition of equilibrium between isomers is set up by the addition of alkali, its appearance cannot well be associated with the occurrence of reversible isomeric change.

No marked change is seen in the absorption spectrum of α -bromo-camphor when a halogen is introduced into the β - or π -position, but the band is no longer developed when the second α -hydrogen atom is displaced by a halogen or by a nitro-group; it may therefore be associated with the presence of a displaceable hydrogen atom in the group $-\text{CHX}\cdot\text{CO}-$, although not dependent on any actual transference of the atom; α' -bromo- α -methylcamphor appears, however, to produce a shallow band.

The weak band of nitrocamphor is greatly intensified by alkalis, but does not appear in the spectrum of the anhydride derived from the pseudo-form; it is therefore dependent on the presence of a displaceable hydrogen atom rather than on the occurrence of a pseudo-nitro-structure. The β - and π -bromo-derivatives behave like nitrocamphor, but the α -halogen derivatives, which do not undergo isomeric change in solution, produce no absorption band. Nitrocamphane does not give rise to a band either alone or in presence of alkali.

9. *The Relationship between the Constitution and the Absorption Spectra of Pyridine and various Derivatives.* By JOHN EDWARD PURVIS.

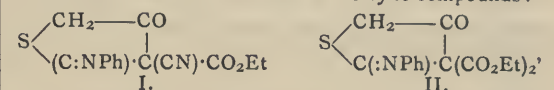
The absorption bands of 3:5-dichloropyridine, two isomeric trichloropyridines, two isomeric tetrachloroaminopyridines, α -picoline and several of its derivatives, 2:4:6-trimethylpyridine and several of its derivatives, and chlorolutidine have been investigated.

The results showed that:—(1) The general effect of introducing atoms or groups of atoms into the nucleus is to increase the persistence of the absorption band as well as to shift it towards the red end of the spectrum, whilst when they are introduced into the side-chains they generally decrease the persistence. (2) The weighting of the nucleus does not, however, always mean that the absorption band is shifted towards the red end. The type and the spatial position of the introduced atoms or groups are factors in determining the absorption. (3) In isomeric substances, the spatial positions of the substituting atoms in the nucleus are of considerable importance in influencing the position and the persistence of the absorbed rays. (4) The substitution of atoms in the side-chains does not exert the same marked influence as when they are substituted in the nucleus. (5) The addition of hydrochloric acid to 2:4:6-trimethylpyridine and α -picoline (as well as to pyridine and lutidine) exerts a marked influence on the vibrations of the nucleus, and the effect is very similar to that produced when chlorine atoms are introduced into the nucleus.

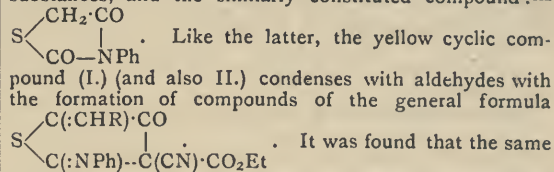
Considerations on the influence of the changing valency of the nitrogen atom and other conditions in explanation of these facts were discussed.

10. *The Action of Mustard Oils on the Ethyl Esters of Malonic and Cyanoacetic Acids.* Part II. By SIEGFRIED RUHEMANN.

The author showed that each of the cyclic compounds:—



which he described recently (*Trans.*, 1908, xciii., 621) as existing in two modifications, namely, a yellow and a colourless one, only occur in one form. He was led to this result in the course of a comparative study of these substances, and the similarly constituted compound:—



Like the latter, the yellow cyclic compound (I.) (and also II.) condenses with aldehydes with the formation of compounds of the general formula

It was found that the same products were formed from the colourless compound, and this fact led to the view that both specimens of I. were identical. The author was able to verify this conclusion.

11. *The Interaction of Hydrogen and Chlorine.* By DAVID LEONARD CHAPMAN and PATRICK SARSFIELD MACMAHON.

The authors have shown that the statement of Bunsen and Roscoe, that the rate of photochemical action between chlorine and hydrogen in a mixture containing equivalent amounts of these gases is reduced by the addition of a small volume either of hydrogen or chlorine, cannot be substantiated. Hydrogen and chlorine prepared by the electrolysis of concentrated hydrochloric acid do not possess the alleged inhibitive influence if sufficient precautions are taken to exclude air. It is considered likely that the hydrogen used by Bunsen and Roscoe contained oxygen. This is the more probable, as the gas employed by them was prepared by the electrolysis of dilute sulphuric acid.

12. *Nitrogen Chloride.* By DAVID LEONARD CHAPMAN and LEONARD VODDEN.

The authors have shown by a direct analysis that the amount of hydrogen contained in the vapour of nitrogen chloride prepared by the action of chlorine on a neutral solution of ammonium chloride is inappreciable. In harmony with this result, the ratio of nitrogen to chlorine is

found to agree very closely with the formula NCl_3 . Gattermann's conclusion that the freshly-prepared chloride contains hydrogen which can only be replaced by the continued action of chlorine is therefore called in question.

A method by which the ammonium chloride resulting from the hydrolysis of nitrogen chloride with hydrochloric acid can be isolated without the aid of a reducing agent was described. The method affords the first entirely satisfactory demonstration of the reversibility of the change expressed by the equation $\text{NH}_4\text{Cl} + 3\text{Cl}_2 = \text{NCl}_3 + 4\text{HCl}$.

13. "The Atmospheric Oxidation of β -Methylhydrindone." By ARTHUR HENRY SALWAY and FREDERIC STANLEY KIPPING.

β -Methylhydrindone, $\text{C}_6\text{H}_4\text{<CH}_2\text{>CHMe}$ (Kipping and Clarke, *Trans.*, 1903, lxxiii., 913), is slowly oxidised on exposure to the air, giving a mixture of compounds from which acetic, phthalic, and benzylmethylketone-*o*-carboxylic acid, $\text{CH}_3\text{CO}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, may be isolated; a small amount of a neutral compound, melting at 211° , is also present in the crude oxidation product.

It is suggested that the ketonic form of methylhydrindone (compare Kipping, *Proc.*, 1902, xviii., 34) first undergoes change to the enolic modification, which then combines directly with a molecule of oxygen in much the same way as unsaturated compounds combine with a molecule of ozone; this additive product is then decomposed by water, giving benzylmethylketone-*o*-carboxylic acid, and by similar processes the latter is oxidised to phthalic and acetic acids.

14. "A Glucoside from *Tephrosia purpurea*." (Preliminary Note). By GEORGE CLARKE, jun., and S. C. BANERJEE.

Tephrosia purpurea, Pers. (nat. ord. *leguminosae*), a small woody annual, grows luxuriantly during the monsoon in many waste tracts of the United Provinces of Agra and Oudh. The leaves yield a crystalline glucoside on extraction with either ethyl alcohol or acetone, and subsequently treating the evaporated extract with water and light petroleum to separate tar. The yield from one extraction is approximately 2 per cent on the dried leaves. The glucoside melts and decomposes at $180\text{--}185^\circ$ (uncorr.), and on hydrolysis with dilute sulphuric acid yields quercetin and dextrose. It appears, therefore, to be identical with osyritrin (A. G. Perkin, *Trans.*, 1897, lxxi., 1134).

15. "Note on the Constitution of the Carboxyl Group." By IDA SMEDLEY.

From a consideration of the physical and chemical properties of the carboxylic acids, the constitution $\text{C}\begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{OH} \end{smallmatrix}$

is suggested for the carboxyl group as better representing its physical and chemical behaviour.

16. "The Relation between the Chemical Constitution and Optical Properties of the Aromatic α - and γ -Diketones." By IDA SMEDLEY.

Yellow *s*-dibenzoyl ethylene (m. p. 111°) was prepared by condensing benzoyl formaldehyde with acetophenone in the presence of acetic anhydride. This compound is identical with that obtained by Paal and Schulz (*Ber.*, 1900, xxxiii., 3784) by the action of heat on dibenzoylmaleic acid. From a consideration of the solubility, melting-point, refractive power, and colour of the *cis*- and *trans*-isomerides, the yellow form, which has the greater solubility, lower melting-point, and greater refraction, is regarded as the *cis*-isomeride, and not the *trans*-form as suggested by Paal and Schulze. These two forms furnish the first instance described of a marked difference in the refraction of *cis*- and *trans*-isomerides. The molecular refractions of the following compounds were measured:—Phenyl methyl diketone ($M_a = 41.32$), benzoyl formaldehyde ($M_a = 36.99$), *cis*-dibenzoyl ethylene (m. p. 111° ; $M_a = 73.96$), *trans*-dibenzoyl ethylene (m. p. 134° ; $M_a = 71.84$), *cis*-dibenzoyl phenylethylene ($M_a = 99.57$), *cis*-dibenzoyldiphenylethylene ($M_a = 122.76$), *trans*-diben-

zoyldiphenylethylene ($M_a = 123.71$). The evidence from a consideration of their refractive power is applied to determine the constitution of the α diketones and *s*-diacyl ethylenes. Marked similarities are shown in the behaviour of these two classes of compounds.

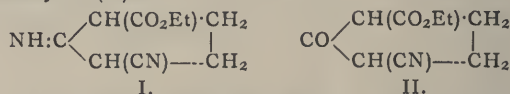
17. "The Transformation of Aliphatic Nitriles into Alicyclic Imino-compounds." (Preliminary Note). By JOCELYN FIELD THORPE.

For some time past experiments have been in progress having for their object the study of the conditions under which aliphatic dinitriles having the nitrile groups separated by two, three, four, &c., carbon atoms pass into the corresponding alicyclic imino-compounds.

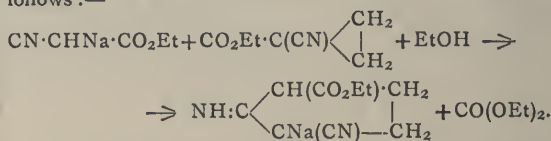
Preliminary experiments indicate that there is a greater tendency to form a three-carbon ring in this manner than a ring of four carbon atoms, but that the cyclopentane ring is produced with most remarkable ease.

Thus, during some experiments on the formation of the cyclopropane ring by the interaction of ethyl sodiocyanoacetate and ethylene dibromide, Carpenter and Perkin (*Trans.*, 1899, lxxv., 921) isolated, as a by-product, a substance which melted at 119.5° , and to which they assigned the formula $\text{CN}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$ (ethyl $\alpha\delta$ -dicyanovaleate), owing to the fact that it yielded adipic acid on hydrolysis with alkaline hydrolysing agents.

It is now found that this substance is ethyl 2-imino-3-cyanocyclopentane-1-carboxylate (I), and that it is immediately converted by the action of cold concentrated hydrochloric acid into ethyl 3-cyanocyclopentane-2-one-1-carboxylate (II).—



Ethyl 2-imino-3-cyanocyclopentane-1-carboxylate can be produced in almost theoretical yield by the interaction of ethyl sodiocyanoacetate and ethyl 1-cyanocyclopropane-1-carboxylate in alcoholic solution, the sole products of the reaction being the sodium compound of the imino-compound and ethyl carbonate; the equation representing the initial and final products of the reaction is therefore as follows:—



A similar condensation product is obtained when ethyl sodiomalonate is substituted for ethyl sodiocyanoacetate in the above equation. The investigation of the properties of these cyclic ketones is in progress.

18. "Action of Alcohols on Metallic Calcium." By FREDERICK MOLLWO PERKIN and LIONEL PRATT.

When calcium is added to alcohols reaction ensues and the alkoxide, $\text{Ca}(\text{OAlk})_2$, is produced (*Proc.*, 1907, xxiii., 304). The reaction, however, is generally slow, but is greatly facilitated by heat. Calcium hydride reacts more readily than metallic calcium, but the product is less pure than when the metal is employed, owing to impurities in the calcium hydride. Calcium ethoxide is soluble in ethyl alcohol, and crystallises with two molecules of alcohol of crystallisation. Other alkoxides are not so readily prepared, owing to their insolubility in the alcohols. Calcium ethoxide has been employed satisfactorily for organic condensations in place of sodium ethoxide.

19. "The Condensation of Oxymethylene camphor with Primary and Secondary Amino-compounds." By WILLIAM JACKSON POPE and JOHN READ.

On condensing externally compensated α -phenylethylamine with *d*-oxymethylene camphor, two stereoisomeric products are obtained, one from each of the optically

active components of the primary base; a method is thus indicated for ascertaining whether a particular primary amino-compound is or is not externally compensated. The two products exhibit marked mutarotation, and this is attributed to their conversion in solution into isodynamic mixtures.

o-Xymethylenecamphor itself and its condensation products with aniline, *p*-toluidine, and β -naphthylamine exhibit mutarotation in various solutions, and this is again attributed to isodynamic change.

20. "Note on the Variation in the Catalytic Activity of Mineral Acids with Changes in their Concentration." By ARTHUR LAPWORTH.

Several recent investigations (Senter, *Trans.*, 1908, xci., 467; Stieglitz, *Am. Chem. Journ.*, 1908, xxxix., 29 *et seq.*; Acree and others, *Ber.*, 1908, xli., 3214 *et seq.*) suggest that during certain changes, in which electrolytes are concerned, not only simple and complex ions are directly concerned, but that intramolecular changes in, and interactions between, non-ionised substances may occur, and sometimes even to the extent of being a necessary part of the process.

The author recently referred to such a possibility in the case of esterification as accelerated by an acid (*Trans.*, 1908, xciii., 2196, 2197), inferring that the disproportionate increase in the velocity with increase in the amount of mineral acid may possibly be due to a secondary reaction of this nature. It is necessary to state that the discussion applied only to those cases where no relatively powerful base is present in such small quantity that this decreases rapidly on addition of mineral acid, as might conceivably be the condition in alcohol containing only a very little water; the general case, however, comes under the discussion mentioned, and, as has long been recognised, is doubtless intimately connected with neutral salt action.

Attention must also be drawn to the fact that the expression for $\frac{1}{2} \frac{d^2(H^2)}{dA^2}$ (not $\frac{d^2(H^2)}{dA^2}$; *loc. cit.*, p. 2197),

which indicates the direction of change in relative quantity of non-ionised compounds with alteration in the amount of catalyst, is always positive, this not being limited even by the condition suggested.

21. "The Condensation of Dimethyldihydroresorcin with Ethylamine." By PAUL HAAS.

By the action of nitrous acid on the condensation product of ethylamine with dimethyldihydroresorcin, a compound of the constitution $\text{CMe}_2 \begin{array}{c} \text{CH}_2 \cdot \text{C}(\text{:NEt}) \\ \text{CH}_2 \text{---CO} \end{array} \text{C:N:OH}$ is produced.

This substance crystallises from water with two molecules of the solvent, and has a very intense carmine colour; when dried in a vacuum it becomes anhydrous, and is then dark blue.

SOCIETY OF CHEMICAL INDUSTRY.

(LONDON SECTION).

Ordinary Meeting, February 1st, 1909.

Dr. J. LEWKOWITZSCH in the Chair.

"Gun-cotton and its Manufacture." By Colonel Sir FREDERIC L. NATHAN, R.A.

Gun-cotton was discovered by Schönbein in 1846. Its manufacture was worked out by Von Lenk and improved by Abel. The raw material is cotton-waste; this is immersed in small quantities for a few minutes in a mixture of nitric and sulphuric acid, the excess acid squeezed out, and nitration completed in earthenware pots. The acid is removed by centrifugalising, the gun-cotton drowned in water, and purified by boiling, pulping, and washing.

The nitration process has been modified of late. In one case the nitration is completed in the original dipping-pan, in another it takes place in the centrifugal itself. A third process, the Thomson displacement process, was introduced

recently at Waltham Abbey. The nitration is effected in shallow circular earthenware pans; when it is finished, water is run slowly into earthenware plates placed on top of the cotton, and a cock at the bottom of the pan is opened for the waste acid to run out at the same rate as the water runs on. The water removes the acid from the gun-cotton which is ready for boiling. This process has many advantages over the others. The paper describes fully all the operations in the manufacture of gun-cotton.

THE RÖNTGEN SOCIETY.

At the February meeting of this Society Dr. A. H. PIRIE initiated a Discussion upon the question of the Transport of Ions. He said that the first to use ionic medication in this country was Benjamin Ward Richardson, but that it was only within the last ten years that the method had become popular in the treatment of certain diseases. The possible modes of conduction of electricity had been divided by Sir Oliver Lodge into the birdseed method, the bullet method, and the fire-bucket method. In the case of the introduction of ions into the human tissues, the first of these methods was the one which had to be considered. As a bird carried a seed with it and only dropped it when it had reached its destination, so an ion carried its electric charge—the smallest known portion of electricity—and dropped it when it reached an electrode. Chemical, toxic, antiseptic, and medicinal actions of electrolytic substances were almost exclusively ionic in nature. Toxic and pharmacological actions depended essentially on ionic groups, and it was much more important therapeutically to consider the ionic group than the atomic or molecular. As an example, he took phosphides and phosphates. The first were toxic, the second were not. Phosphides, though united to cations which had different actions, all possessed the same toxic and therapeutic effects. The phosphorus ion was all important in the phosphides. The phosphate molecule contained phosphorus in the same proportion as did the phosphide, but the phosphorus in the phosphate was locked up in the complex ion, PO_4^{3-} , the properties of which were quite different from the phosphorous ion of the phosphides. The same could be said of sulphates and sulphides, and, in general, of all ions. When a current passed through the human body there was an exchange of ions between the surfaces of contact of dissimilar chemical compounds. The anions in the depth of the tissues moved towards the positive pole, and the cations moved towards the negative pole, and there was thus a change in the chemical composition of the deep tissues of the body. After demonstrating the manner in which different ions entered the skin, Dr. Pirie said that the chief disadvantage of using ions in medicine was the fact that it was only possible for the patient to bear a comparatively small current with any degree of comfort. Usually this amounted to about 1 milliampère per square centimetre.

In the subsequent discussion Dr. LEWIS JONES read a letter he had recently received from Professor Leduc, of Nantes, the pioneer of recent ionic medication, in which the French investigator pointed out a curious effect he had lately obtained on applying an electrode of metal to a surface of gelatin. A film of gelatin, impregnated with ferrocyanide of potassium, is taken upon glass, and metallic electrodes, which may be of copper, iron, or zinc, are laid down side by side at convenient distances from this conducting film. A migration of ions then takes place, forming a precipitate of ferrocyanide of copper or iron or zinc, as the case may be. But, strangely enough, the current does not pass evenly, but shows a tendency to concentrate around the edges of the electrode. Thus the gelatin surface immediately under the electrode does not receive the same share of current as the portions corresponding to the edges. The ferrocyanide of copper marks the distance that the copper ions move during the experiment, and several slides were shown in which a greenish

patch in the gelatin was seen to be surrounded by a ring of brown, due to the ferrocyanide. The gelatin immediately under the electrode remained green, while the parts near the periphery of the electrode became coloured brown.

NOTICES OF BOOKS.

Quantitative Experiments in General Chemistry. By JOHN TAPPAN STODDARD. New York, London, Bombay, and Calcutta: Longmans, Green, and Co. 1908.

THERE is a good deal to be said for the contention of the author of this book, that the average student of chemistry will get a better grasp of the principles of the science if his experimental work is made as quantitative as possible, and if, moreover, instead of performing a very few refined and perfectly accurate determinations he aims rather at carrying out a comparatively large number of estimations by methods which are above all rapid, even if rough. Acting upon this view the author gives a rather unusual course of practical work, and describes a number of determinations very briefly. In addition the gas laws are studied, methods of determining the densities of gases are described, and the composition of water and air are treated. Some volumetric work is also included, and a specific heat determination. When it is mentioned that all this material occupies only a hundred small pages, it will be seen that brevity and conciseness must have been made special features of the descriptions, and the reviewer's attention would naturally be directed towards the detection of cases in which accuracy has been sacrificed or important details have been omitted. Such failings, however, are not apparent, and the course of practical work given in the book should make the student quite familiar with all the ordinary operations of practical chemistry and with the usual forms of apparatus, and at the same time lead him to obtain numerical data upon which to base the laws of chemical combination.

Metallic Alloys; their Structure and Constitution. By G. H. GULLIVER, B.Sc., F.R.S.E., A.M.I.Mech.E. London: Charles Griffin and Co., Ltd. 1908.

IN this book, which is based upon the lectures on alloys delivered in the Engineering Department of the University of Edinburgh, the theory of alloys is treated systematically. Methods of investigating them with the microscope, &c., are first described in an introductory chapter, which is of a more practical character than the rest of the book. The theory of solutions and chemical equilibrium are then taken up, and the case of binary alloys is considered in comparatively full detail. Although, of course, it has been found quite impossible to include accounts of all the work upon the formation of definite compounds in alloys which is issuing with such rapidity, especially from French laboratories, the author has done the best he can in this respect, choosing the brasses and bronzes for fullest treatment. The iron-carbon alloys and steels are purposely considered somewhat briefly, because books dealing exclusively with them are easily procurable. The phase rule also is treated rather shortly, no attempt being made to discuss the thermo-dynamical basis of the rule, for which the student is recommended to refer to special treatises on the subject.

Text-book of Botany and Pharmacognosy. By HENRY KRAEMER, Ph.B., Ph.D. Third Edition. Philadelphia and London: J. B. Lippincott Company.

IN the third edition of this book many alterations have been made in the illustrations, the half-tone photographs being replaced by line drawings, in which not only the external morphological characters but also the internal structures of the specimens are made clear. Some new illustrations

for instance, those of solanaceous drugs, have also been added. The third part of the book on Reagents and Microtechnique has been extended, and a few further additions have been made. The best proof of the value of the work for students of botany and for drug analysts is to be found in the fact that it has been necessary to produce a third edition within a very short time after the appearance of the second, which again followed quickly on the first.

MISCELLANEOUS.

Anniversary Dinner.—It has been decided by the Council to arrange for a Dinner of the Fellows of the Chemical Society and their friends, to be held at the Whitehall Rooms on Thursday, March 25th, 1909, this being the day fixed for the Annual General Meeting. Further particulars will be announced shortly.

Royal Institution.—On Thursday next, February 18, at 3 o'clock, Dr. Hans Gadow will begin a course of three lectures at the Royal Institution on "Problems of Geographical Distribution in Mexico." The Friday Evening Discourse on February 19 will be delivered by Sir Henry Cunynghame on "Recent Advances in Means of Saving Life in Coal Mines."

MEETINGS FOR THE WEEK.

- MONDAY, 15th.—Royal Society of Arts, 8. (Cantor Lecture). "Modern Methods of Artificial Illumination," by Leon Gaster.
- TUESDAY, 16th.—Royal Institution, 3. "Architectural and Sculptural Antiquities of India," by Prof. A. A. Macdonell.
- WEDNESDAY, 17th.—Royal Society of Arts, 8. "The Commercial Relations of France and Great Britain," by Mons. Yves Guyot.
- Microscopical, 8. "On a German Silver Powell Portable Microscope made in 1850," by A. A. C. E. Merlin. "The 'Red Snow' Plant, *Sphaerella nivalis*," by G. S. West.
- THURSDAY, 18th.—Royal Institution, 3. "Problems of Geographical Distribution in Mexico," by Hans Gadow, F.R.S.
- Chemical, 8.30. "A Study of some Asymmetric Compounds," by F. S. Kipping. "Decomposition and Sublimation of Ammonium Nitrite under Heat," by P. C. Ray. "Estimation of Hydroxyl Derivatives in Mixtures of Organic Compounds" and "Simple Method for Determining the Chemical Affinity of Organic Substances," by H. Hibbert. "Isolation of the Aromatic Sulphinic Acids," by J. Thomas. "Analytical Investigation of Zirconium Metal" and "Chlorine Generated by Potassium Permanganate, its Preparation and Purity," by E. Wedekind and S. Judd Lewis.
- FRIDAY, 19th.—Royal Institution, 9. "Recent Advances in Means of Saving Life in Coal Mines," by Sir Henry Cunynghame, K.C.B.
- SATURDAY, 20th.—Royal Institution, 3. "Chamber Music," Sir Alexander C. Mackenzie. (With the kind assistance of the Hans Wessely Quartette).

METROPOLITAN BOROUGH OF DEPTFORD.

APPOINTMENT OF PUBLIC ANALYST.

The Council of the above Borough invites applications for the position of PUBLIC ANALYST for the Borough from gentlemen possessing the necessary qualifications and able to furnish such proof of competency as may from time to time be required by the Local Government Board.

The appointment will be for twelve months from March 31st, 1909, and will be subject to the approval of the Local Government Board.

The fee to be paid for each analysis will be at the rate of Ten Shillings per sample, which is to include the provision of the necessary laboratory, apparatus, and appliances.

Not less than 300 samples will be submitted during the year.

Applications, accompanied by copies of not more than three recent testimonials, and giving particulars of Certificates and Diplomas possessed by the applicant, must be made upon forms to be obtained at the Town Hall, New Cross Road, S.E., and must be returned to the undersigned not later than Saturday, FEBRUARY 27th, 1909.

Canvassing members of the Council, either directly or indirectly, will disqualify candidates.

(Signed) VIVIAN ORCHARD, Town Clerk.

Town Hall, New Cross Road, S.E.,
February 11th, 1909.

THE CHEMICAL NEWS

VOL XCIX., No. 2569.

SCANDIUM.*

PART I.—THE SEPARATION OF SCANDIUM FROM
WOLFRAMITE FROM ZINNWALD.

By R. J. MEYER.

Historical.

In the year 1879 Nilson (*Ber.*, xii., 550, 554, March 22, 1879), who was preparing pure ytterbium, discovered by Marignac, by the fractional melting of the nitrates of the earths from gadolinite and euxenite, discovered a new earth which was present in small quantities in the ytterbium fractions. It was distinguished from the ytterbium earths by the readiness with which its nitrate decomposed on being heated—it was thus more electro-negative than they—and by its very low molecular weight. Thalén's examination of the spark spectrum in the optical region showed that a new element was present. Nilson named it scandium. However, he only succeeded in obtaining about 0.3 grm. of a product in which ytterbium still preponderated; its atomic weight was about 90. Some weeks later, Cleve (*Bull. Soc. Chim.*, [2], xxxi., 486, May 13, 1879) announced that he also had succeeded in isolating scandium, both from gadolinite and from yttriotitanite (keilhauite). The yields first given by him of 0.02 to 0.04 per cent relate, however, to an oxide, which Nilson afterwards calculated to contain only about 30 per cent of scandium earth, while the actual amount present in the minerals worked up by Cleve was estimated to be about 0.002 to 0.003 per cent. Subsequently, Cleve, working with richer raw material, succeeded in obtaining a rather larger amount of the earth in an approximately pure state; he determined its atomic weight with some degree of accuracy, and by preparing some of its compounds he was able to give some description, if incomplete, of the properties of the element. In two determinations he obtained for the atomic weight $Sc = 44.91$ and 45.12 . This discovery was regarded as the more striking because Mendeleeff (*Lieb. Ann.*, Suppl., viii., 133) had foretold the existence and the properties of a new element of atomic weight 44, ekaboron, basing the prophecy on his law of periodicity, and by the fulfilment of the prediction by the experimental discovery the position of scandium in the Periodic Table was settled once for all. In 1880 Nilson published what were for the time being the final statements on the subject (*Ber.*, xiii., 1439, June 12, 1880; *Ofvers af K. Svenska Vet. Akad. Förhandl.*, 1880, No. VI.). He had succeeded in isolating from 10 kilograms of euxenite some grms. of scandium oxide of a high degree of purity; he had also acquired further knowledge of its chemical properties, and had finally established its atomic weight by four determinations which gave the values 43.99 , 44.07 , 44.05 , and 44.02 . (By studying the arc spectrum Exner and Haschek showed that Nilson's preparations contained small amounts of ytterbium). The spark spectrum of this pure material was measured by Thalén (*Comptes Rendus*, xci., 45).

The investigation of scandium was then compulsorily abandoned for a time, and hardly any mention is made of it in literature during the period from 1880 to 1907. Two explanations may be given for this neglect of a substance which had been shown by its discoverers to be highly interesting; owing to its extreme rarity investigators could hardly hope to be rewarded by appreciably increased yields for the considerable outlay of time, trouble, and

money required for the preparation even of small quantities, and, secondly, because searches had often been made for scandium without success. Thus, Urbain mentions that he had never come across scandium in the course of his successful studies, extending over years, of the yttrium earths of various origins (*Journ. Chim. Phys. Gèneve*, 1906, iv., 31). In the current year Sir William Crookes published a preliminary communication on the occurrence of scandium and on the composition of a series of its compounds (*Proc. Roy. Soc.*, lxxx., A, p. 516, June 10, 1908). By the spectrographic examination of fifty-three minerals which almost all contained the rare earths as the basic chief constituent, he showed that ten of them contained scandium, but that only one, namely, wilkite, a Finnish mineral never before described, contained the surprisingly large proportion of 1 per cent scandium oxide, while the other nine contained less than 0.01 per cent. According to the provisional analysis given by Sir William Crookes, the composition of wilkite is very complicated. The negative constituents it contains are titanic, tantallic, niobic, and silicic acids, and the positive constituents are iron, yttrium earths, cerium earths, thorium, uranium, and 1.17 per cent scandium oxide. The mineral must thus be allied to the members of similar composition of the group to which fergusonite, yttriotantalite, samarskite, polycrase, euxenite, &c., belong. For the present no information is given relating to the difficult process of isolating pure scandium from this mineral, nor to its distribution, but, on the other hand, a large number of scandium salts are classified according to their composition.

Quite recently, G. Eberhard published a much more comprehensive account of the occurrence of scandium (*Sitzungsber. Kgl. Preuss. Akad. Wissensch.*, 1908, xxxviii., 851). Starting from the fact that the strongest lines of the scandium spectrum are observed in the spectra of stars in the most different stages of development, he concluded that scandium must be universally distributed on the earth (the same reasoning foretells the occurrence of helium on the earth), and by investigating the arc spectrum of 366 minerals and rocks he obtained the remarkable result that scandium in small quantities is actually one of the most widely distributed of the elements on the earth, and that by spectral methods it may be detected in almost all the rocks which form the earth's crust. He further showed that it is most frequently met with in zirconium minerals, beryls, titanates, niobates, and titan-niobates of the rare earths, in micas, and finally—and this is the most important result from a chemical point of view—that wolframite and tinstone from some places in the mountain ranges of Saxony and Bohemia contain scandium in such amounts that the extraction of the earth from these minerals would be profitable. Undoubtedly the disadvantage of the always small absolute amount of rare earths which these minerals contain, and which has hitherto quite escaped detection by chemical analysis, is outweighed by the fact that scandium forms the predominant constituent of the rare earths generally present in them, while the minerals worked up by Nilson and Cleve contained only traces of scandium distributed throughout an enormous excess of other earths.

So if starting from our fundamental cosmogenetic theories we arrive at a practical result, it may also be foreseen from purely chemical considerations that scandium is not to be searched for specially in the places where it has hitherto been supposed to exist exclusively, namely, in the typical minerals of the rare earths, for the chemical character of the element, so far as it is known at present, deviates considerably from the typical nature of the rare earths in the narrower sense. Such a difference may be confidently expected owing to the low atomic weight; *i.e.*, the position it occupies in the Periodic System. Whereas in the case of the cerium and yttrium earths we are dealing with comparatively strongly positive elements, as we pass from the ytterbium earths, the most negative members of the yttrium earths, to scandium, we observe an unusually decided decrease of basicity. This is shown both by the

* *Zeitschrift für Anorganische Chemie*, lx., 134, November 17, 1908.

ready solubility of the hydroxide and the salts in soda, and by the strongly developed tendency, connected with it, of undergoing hydrolysis and forming complexes. In this respect, scandium is much more like tetravalent thorium, aluminium, or beryllium than the rare earths. Moreover, in other respects, scandium differs from the series of the cerite and yttrium earths. While in the latter the solubility of the oxalates in acids increases with the increasing positive character, the solubility of scandium oxalate far exceeds that of the oxalates of the other earths. Scandium is also distinguished from the other rare earths by the fact that the sulphate crystallises with six molecules of water, a type which is otherwise hardly known amongst the sulphates of the rare earths, and that it is easily soluble in water.

(NOTE.—Brauner appropriately calls scandium "an extrapolation" in the series of the elements of the rare earths (Abegg, "Handb. d. Anorg. Chem.," III., i., p. 340). If it is included amongst the cerium earths because of the difficulty with which its potassium double sulphate dissolves, then it occupies the same isolated position in this sub-group as yttrium in the group of the yttrium earths).

The results obtained by Eberhard do not enable us to detect an evident connection between the chemical nature of scandium and its occurrence on account of its very wide distribution, but it is clear that the occurrence of the element is not restricted to the typical minerals of the rare earths. As regards the occurrence in wolframite and tinstone from the Ore Mountains, this localisation in a small region shows that specific geological causes are responsible for the concentration of the element in this place.

For the investigation now to be described of the quantitative isolation of scandium from wolframite, it seemed desirable to acquire a knowledge of the most important reactions of the element from personal observation. I owe hearty thanks to Prof. Dr. W. Nernst, who enabled me to do so by sending me one of Cleve's original preparations. I should not have been able to carry through this task with any hope of success if the best procedure had not been pointed out by the spectrographic examination of almost all the precipitates and filtrates which were obtained in the numerous attempts to find the most advantageous method. These tedious examinations were very kindly performed by Prof. Dr. G. Eberhard, of the Astrophysical Observatory, in Potsdam. He used for the purpose a grating spectrograph belonging to the observatory (*cf.* G. Eberhard, *loc. cit.*). I wish to express to him also my hearty thanks for this valuable aid, which was indispensable for the success of the work.

Preliminary Experiments.

For the preliminary experiments I obtained from the Department for the sale of minerals of the Kgl. Sächs. Bergakademie, in Freiberg, wolframite from Zinnwald, near Attenberg, in the Saxony Ore Mountains; it consisted of large pure pieces containing only very little matrix. The quantitative analysis of the mineral will be published in a later communication. It was first necessary to ascertain into which part the scandium would go when the mineral was opened up with soda. *A priori* it was to be expected that when the melt was extracted with water the scandium would go over into the alkaline solution with the tungstic acid, since it forms soluble double carbonates. However, when the oxides which remained undissolved on extraction with water were subjected to spectroscopic examination, it was found that they contained all the scandium, while the alkaline filtrate, from which the tungstic acid was separated in the usual way, contained none at all. This behaviour was explained by an observation made later, that solutions of scandium salts in soda, if they are diluted with water and boiled, undergo a complete hydrolytic dissociation with separation of the carbonate. The assumption which was first made, that wolframite possibly contains scandium in the form of a fluoride insoluble in alkali, was not confirmed, for the

examination for fluorine gave a negative result. The examination for fluorine was performed by K. Daniel's very sensitive method (*Zeit. Anorg. Chem.*, 1904, xxxviii., 257). Thus the working up experiments could now be restricted to the residue consisting chiefly of iron and manganese oxide.

Raw Material.

In the first experiments the methods of isolating the scandium quantitatively were worked out. For this purpose the above mentioned very pure wolframite was used; it was finely powdered, and portions of 100 grms. were heated in Chamotte crucibles in a Perrot's furnace with 220 to 230 grms. of free soda, some potassium nitrate being added. The melt was washed with boiling water containing some alcohol, and the brown mixture of oxides left was dissolved in concentrated hydrochloric acid, after having been washed. The silica which separated was removed, the solution was evaporated to dryness on the water-bath, and the residue taken up with water. More recently, after the completion of the preliminary experiments, a manufactory which is engaged in the preparation of metallic tungsten placed at my disposal large quantities of oxide residues from Zinnwald wolframite. These residues from the manufacture of tungsten provide an excellent and cheap raw material for the preparation of scandium, but they can only be used for this purpose if they have been obtained from good ore ("Stuferz"), while the so-called "Setz" or "Schlicherz" (small ore or slick), which contains large quantities of gangue, gives a less productive oxide residue. Even the best ore often contains some matrix, and the residues yield large quantities of silica when they are dissolved in hydrochloric acid. It was usually found that 20 per cent by weight of this "technical wolframite oxides" is insoluble, a circumstance which must be taken into consideration in calculating the yield. I must again point out that only the wolframite from some places in the Saxon and Bohemian Ore Mountains is worth working up for scandium. Eberhard has proved spectrographically that specimens from other places only contain traces of it. I obtained the same result by working up the residues of an Australian wolframite, which gave a yield of only 0.015 per cent of rare earths, while the normal yield of residues from Zinnwald wolframite amounts to 0.30 to 0.33 per cent.

METHODS OF SEPARATION.

I will now describe the methods which lead to the separation and preparation in the pure state of scandium from the solution of wolframite oxides. The chief aim of these experiments was to obtain a "quantitative" isolation, which could only be attained if each precipitation was controlled by means of spectrographic examination.

A.—Concentration by Precipitation with Oxalic Acid.

It is well known that the group of the rare earths is usually totally separated from other substances, such as iron, manganese, calcium, &c., by precipitation with oxalic acid from acid solution. But it must be remembered that scandium oxalate, unlike the oxalates of the other rare earths, is very readily soluble in acids, and that it is impossible to precipitate with alkali oxalates owing to the formation of soluble oxalate complexes. Moreover, the large quantities of iron which the solution contains have a disturbing effect on the separation. When oxalic acid is added to concentrated ferric solutions, the ferric ion, Fe^{+++} , yields a complex ferric-oxalate ion, as shown by the colour change to green. Thus the solution uses up oxalic acid until all the iron is bound in the complex. At the same time the concentration of the H-ions is continually raised. When to the neutral or feebly acid solution of the wolframite oxides a certain quantity of oxalic acid is added, at first no precipitate is formed, but when the solution is warmed or it has stood for a long time, a precipitate appears owing to the formation of ferrous ions by auto-reduction, the latter being gradually separated as difficultly

soluble ferrous oxalate. The scandium is, of course, concentrated in these precipitations of ferrous oxalate, as spectrographic examination shows, but it is not possible to concentrate the whole amount in one fraction by this method; nor can this be effected if the iron solution is first reduced with sulphurous acid and the ferrous oxalate is then precipitated in fractions by successive additions of oxalic acid. An almost complete precipitation of the rare earths may be accomplished if to the nearly neutral ferric solution a sufficient excess of oxalic acid is added to bind all the iron in the solution in an oxalate complex; then further addition of the acid precipitates scandium oxalate. The weight of oxalic acid necessary is nearly the same as the weight of oxides used. Since, owing to the solubility of scandium oxalate in acids, the iron solution must be as nearly as possible neutral before the precipitation, and the complete evaporation of solutions, from which large quantities of iron chloride separate, is accompanied by difficulties when considerable quantities of wolframite oxides had to be worked up, an approximately saturated solution was first prepared. For this purpose 1 kilogram of the oxides was boiled with 2.5 litres of crude hydrochloric acid (sp. gr. 1.16) until no more chlorine was evolved. The solution was then diluted a little, and the dark red iron solution was drawn off from the deposit of silica. The latter was boiled with water and washed, the filtrate being added to the first filtrate. (This insoluble residue persistently retains soluble constituents; it should be quite grey after washing). This solution, the volume of which was about 3 litres, was neutralised by the addition of concentrated ammonia (25 per cent) drop by drop, the whole being vigorously stirred until a permanent precipitate was formed. (For this purpose about 200 cc. NH_3 are necessary for every kilogram of oxide used). Then a hot saturated solution of 800 grms. of oxalic acid was added. After standing for twenty-four hours a greyish yellow or yellow precipitate containing some crystals of oxalic acid separated. This consisted of a mixture of manganese, calcium, lead, and iron oxalates, as well as the oxalates of the rare earths which are completely precipitated in these circumstances. After washing and igniting the oxalates a mixture of oxides, coloured black by manganese dioxide, remained, its weight being 4 to 5 per cent of that of the oxides used. By this method a very considerable concentration of the earths is effected. It is not practicable to prepare them in the pure state from this mixture, because of the impossibility of completely removing the manganese. The lead was removed with sulphuretted hydrogen, the calcium with ammonia, and the hydroxides were dissolved in hydrochloric acid. (Spectrographic examination shows that the lead sulphide always contains scandium). Then the neutral solution of the chlorides was again precipitated with an excess of oxalic acid. But in this process the manganese always follows the earths, and cannot be completely removed by repeated precipitations of oxalate from faintly acid solution. (I have often observed in other cases the pertinacity with which manganese follows the rare earths; for instance, it is exceedingly difficult to remove manganese completely from manganese double nitrate fractions of the cerium earths). However, after many unsuccessful experiments it was found that the separation could easily be effected by precipitating the earths with hydrofluoric acid.

(To be continued).

South-Western Polytechnic Institute, Chelsea.—Professor Henry A. Miers, D.Sc., F.R.S., Principal of the University of London, presents prizes and certificates to Students of Evening Classes and Day College on March 12th, at 8 p.m.

Aqueous Solutions of Pyridine.—E. Baud.—Aqueous solutions of pyridine contain at least two hydrates, the one containing $2\text{H}_2\text{O}$ and the other $6\text{H}_2\text{O}$ to one molecule of pyridine. At the ordinary temperature these hydrates are dissociated in their solutions. The hydrate containing the most water is the least stable.—C. R., cxlviii., No. 2.

A SIMPLE METHOD FOR DETERMINING VAPOUR-DENSITIES.

By PHILIP BLACKMAN.

THE following method for obtaining the necessary formula for the calculation of vapour-densities will be found much more satisfactory than (it also differs in the latter part from) the incomplete one given in the *CHEMICAL NEWS*, 1907, xcvi., 223, or the fragmentary one given in the *Zeit. Phys. Chem.*, 1908, lxiii., 49, 50, 636, especially with regard to the legality of considering L , L_c , l , and l_c as linear quantities (compare also *Journ. Phys. Chem.*, 1908, xii., 662, 668).

Let—

- w = the weight of the substance experimented on,
- t_1° = the atmospheric temperature,
- L = the length of the air-thread in the manometer at t_1° (before sealing the bulb),
- L_c = the length of the air-thread in the manometer at t_1° (after the bulb is sealed),
- l = the length of the air-thread in the manometer at t_2° ,
- V = the volume of the bulb,
- p = the atmospheric pressure,
- d = the vapour-density required.
- t_2° = the temperature to which the bulb is heated,
- H, h = the volumes of the air-thread at t_1° and t_2° respectively between the open end of the manometer and the mercury thread,
- a = the area of the cross-section of the capillary bore.

The initial internal pressure at t_1° —

$$= pLa/L_c a = \psi \dots \dots \dots (1);$$

the final total pressure at t_2° —

$$= \frac{\psi L_c a (273 + t_2)}{la (273 + t_1)} \dots \dots \dots (2);$$

the pressure of the air only in the bulb at t_2° —

$$= \frac{\psi (V + H) (273 + t_2)}{(V + h) (273 + t_1)} \dots \dots \dots (3).$$

The volume of the vapour at 0° and 760 mm. is $11160 w/d$ (assuming that at 0° and 760 mm. pressure 1 gm. of hydrogen occupies 11160 cc.); at t_2° the volume is $V + h$; consequently its pressure is—

$$\frac{11160 \times 760 w (273 + t_2)}{273 d (V + h)} \dots \dots \dots (4);$$

but (2) = (3) + (4), from which, on simplification,—

$$d = \frac{31068 w l L_c (273 + t_1)}{p L (V + h) (L_c - l) \frac{V + H}{V + h}}$$

Generally H and h are so small compared with V that they may be neglected, and use be made of the far simpler and almost inappreciably less accurate formula—

$$\frac{31068 w l L_c (273 + t_1)}{p L V (L_c - l)}$$

It is interesting to observe that the less complicated formula may be obtained in the following simple and instructive manner:—

The vaporised substance causes the manometer air-thread to contract by the amount $L_c - l$, which corresponds to a comparative pressure $(L_c - l)/l$, or an actual pressure—since the initial pressure is ψ , see (1) above, and the temperature has altered from t_1° to t_2° —

$$\frac{\psi (L_c - l) (273 + t_2)}{l (273 + t_1)}$$

which, however, must be equal to—

$$\frac{11160 \times 760 w (273 + t_2)}{273 d (V + h)}$$

—see (4) above. Therefore, after simplifying,—

$$d = \frac{31068 w l L_c (273 + t_1)}{p L (V + h) (L_c - l)}$$

In calculating the percentage composition of a binary mixture it may occasionally be found more convenient to use the equation—

$$d_2 w_1 + d_1 (100 - w_1) = 100 d_1 d_2 / d$$

than—

$$d_2 w_1 + d_1 (100 - w_1) = \frac{100 d_1 d_2 p L V (L_c - l)}{31068 w l L_c (273 + t_1)}$$

ackney Technical Institute,
London, N.E.

A CONVENIENT FUNNEL SUPPORT.

By L. D. HAVENHILL.

It frequently happens when a chemist has to make a large number of slow filtrations that he finds himself embarrassed by the lack of a sufficient number of funnel supports. The writer recently overcame an experience of this kind by



FIG. 1.



FIG. 2.

improving a simple and inexpensive holder, which has since proven so convenient, especially for holding small funnels, that he desires to bring it to the notice of his fellow

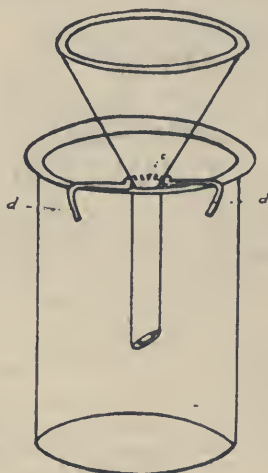


FIG. 3.

chemists and others who may perhaps sometimes find use for it.

For supporting funnels up to 10 cm. in diameter, take a piece of No. 18 copper wire about 10 cm. long and bend it around the stem of the funnel until it assumes the form of a key (Fig. 1). Then open out the arms of this key and bend the ends downwards and inward, so that they will hook over the top of the beaker or other receiving vessel (Fig. 2). The holder rests on the top of the beaker at the points *a a*. The funnel is supported by the loop *c*, which partially encircles the stem and holds it against the inner side of the beaker, as shown in Fig. 3.

A sufficient length of wire should be used in forming the hooks *d d*, so that the support cannot fall into the receiving vessel when the funnel is withdrawn from it. The length and size of the wire, as well as the size of the loop formed around the stem of the funnel, can be varied to suit the size of the funnel as well as the kind of receiving vessel used.—*Journal of the American Chemical Society*, xxxi., No. 1.

A NEW DEVELOPMENT IN GAS HEATING.

THE Bunsen burner, though it has proved its real worth through many decades and is conceived along truly scientific lines, falls short of our ideal.

Some few years ago a French chemical engineer, M. Méker, determined to design a burner which should closely approach the ideal, and after many systematic experiments and much painstaking and persevering work, his efforts were rewarded with success. A sectional view of the final type adopted is shown in Fig. 1.

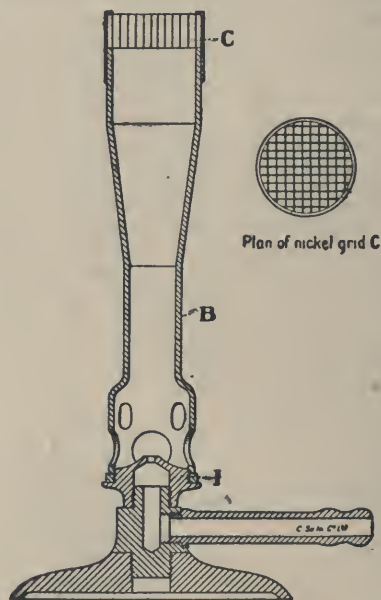


FIG. 1.—ORDINARY MÉKER BURNER.

It will be seen that the gas enters at the bottom of the burner in the usual way, but the air inlet holes are much larger than usual, and the mixing chamber or chimney is of a special shape somewhat resembling an injector. By this means the gas and air are caused to thoroughly mix in the proportions necessary for complete combustion, and the mixture ascends at a great speed. The essential feature of the burner is, however, what M. Méker calls the "cloissonnage" fitted at the mouth of the burner to prevent "back-firing." This is a deep grid built up of thin strips of nickel, and is in appearance somewhat like a honeycomb, except that for simplicity in construction the cells are of square section. This nickel grid completely

covers the mouth of the burner, as will be seen by the plan in Fig. 1, and each of the square channels formed measure 2 millimetres square and is 10 millimetres deep. The fact that this grid is so successful in preventing the flame from gaining entrance to the highly explosive mixture in the mixing chamber or chimney, is because a flame has great difficulty in travelling in a direction opposite to the movement of the gaseous mixture which gives rise to it, if in this inverse direction it encounters a very large cooling surface. Since the grid is of such an open mesh, it has practically no throttling action on the mixture, and being made of nickel it has a great power of resisting oxidation or chemical action, and therefore a long life. Also it acts to some extent as a regenerator of heat, since the heat which is absorbed by the upper surface in contact with the flame is conducted downwards and given up to the cold gaseous mixture as it rises up the channels. The grid is thus always kept at a comparatively low temperature, so that if, accidentally, molten matter falls on it, it immediately solidifies without penetrating the interior and can be readily removed after cooling.

The flame given by the Meker burner is quite novel in appearance and unique in its characteristics. At the top

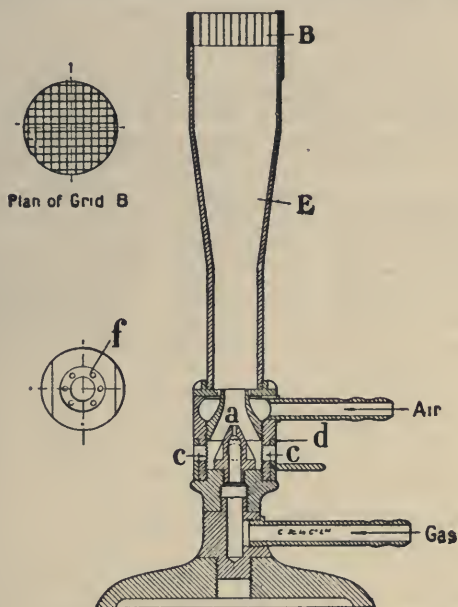


FIG. 2.—MEKER BURNER FOR USE WITH AN AIR BLAST.

of each channel in the grid a small cone about 2 mm. high is visible, but above this is a solid cylinder of flame intensely hot. Experiments with a thermo-couple have shown that the temperature at all points in the flame is practically the same, and is higher than the highest temperature found in the ordinary Bunsen flame. If a thick copper wire be held in the flame it is quickly melted.

Special muffle and tube furnaces have also been made, in which temperatures up to 1200° C. can be obtained, also without any air-blast.

Such striking results at once suggest the question as to what may be expected of this burner when it is intended to use an air-blast. The burner so designed is illustrated in Fig. 2.

It will be seen that the mixing chamber and "cloissonage" remain the same, but the air-blast itself enters by the tube marked "Air" and escapes into the mixing chamber through six small holes arranged concentrically around the gas injector.

These burners and furnaces have up to the present been very little known in England, but we understand that,

under the new Patent Act, they will in future be manufactured here by the Cambridge Scientific Instrument Company, Ltd., of Cambridge, who have acquired the sole rights for Great Britain and the Colonies.

METHOD OF PRODUCING PURE SOLUTION OF THE EFFECTIVE PRINCIPLE OF THE SUPRARENAL GLAND OR PARANEPHROS.

By Dr. MORITZ MAX FREUND.

THIS patented invention relates to a method of producing a pure solution of the effective substance of the suprarenal gland or paranephros. It is known that solutions of the effective substance of the suprarenal gland or paranephros, $C_9H_{13}NO_3$, are very easily oxidised, with accompanying discoloration on coming into contact with air. This applies both to the solutions of the separated substance as well as to raw aqueous extracts of the organ. It has therefore been proposed already to avoid or restrict the oxidation by carrying out the whole operation of extraction under air seal; i.e., excluding the air, or by working in an atmosphere of hydrogen. The effect aimed at, however, could only be obtained to a very imperfect degree or with great difficulty.

I have found that known processes of electrolytic reduction, which effect a rapid and energetic reduction, may be used with advantage for this purpose. I have found that this method or process is applicable both to solutions of the separated substance as well as to aqueous extracts of the suprarenal gland or paranephros, as in both cases no progressive decomposition or change in the substance itself takes place.

This invention consists in preparing a pure solution of the effective principle of the suprarenal gland or paranephros by electrolytic reduction of impure solutions of the substance or its salts.

By this process solutions are obtained which remain for a long time undecomposed, and, further, the base when isolated is both white and analytically pure.

Solutions which contain 3 to 5 per cent of the effective substance $C_9H_{13}NO_3$ are used for reduction. For example, an extract of one-tenth kilogram fresh gland is prepared, the bulk being preferably not greater than 500 cc. This solution is filtered, and then electrolytically reduced, using a platinum cathode, a carbon anode, and a porous cell as a diaphragm. The solution is rendered slightly acid, the duration of the action being preferably from one to two hours. Solutions of salts of the isolated substance may be similarly subjected to electrolytic reduction.

Thus a solution of the hydrochlorate of the isolated substance (say, 20 grms. in 600 cc.) may be subjected to an electrolytic reduction by cathodic hydrogen for one hour as in the above process.

Nitrohydroquinonedimethylether and the Theory of Solutions.—Hugo Kauffmann.—Nitrohydroquinonedimethylether gives colourless or yellow solutions with different solvents. The investigation of this phenomenon shows that change of fluorescence occurs usually without any alteration in constitution, and thus it is not correct to ascribe it to constitution. Even with unalterable constitution there is in the molecule an element capable of being altered; this may be represented graphically by a "condition" formula. The constitutional formulæ are ideal extremes which the condition formulæ more or less approach. The conditions may be deduced from variations in the fluorescence band. Non-dissociating solvents are not indifferent, and allow an approximation to the ideal condition to be attained. The assumption that two modifications of nitrohydroquinonedimethylether exist is unnecessary, the change of colour being due to condition changes.—*Berichte*, xli., No. 18.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 4th, 1909.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President,
in the Chair.

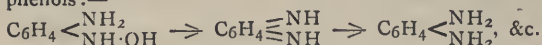
Mr. F. WILLIAMS was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Howard Alfred Caulkin, B.Sc., Oaklands, Solihull, Warwickshire; John Henry Chew, 40, Lytham Road, Blackpool; George Clarke, Cawnpore, U.P., India; George Stanley Cooper, Heaton House, Cleckheaton, Yorks.; William Fowler, 3, Cranbrook Road, Victoria Docks, E.; Egerton Hargreaves, M.Sc., "Arthog," Garner's Lane, Davenport; Reginald Hopkinson, B.Sc., Brimington House, Brimington; Floyd J. Metzger, Columbia University, New York City, U.S.A.; Oswald John Dalgatty Thomas, 65, Clarendon Gardens, Ilford; Vernon James Tilley, "Linthorpe," Beccmead Avenue, Streatham, S.W.; Charles William Truelove, B.Sc., 17, Tylney Road, Forest Gate, E.; Robert William Wilson, 2, Parade, Aldersbrook Road, Manor Park, E.

Of the following papers, those marked * were read:—

*22. "The Mechanism of the Reduction of Nitroanilines and Nitrophenols." By BERNHARD FLÜRSCHHEIM.

Flürscheim and Simon have shown recently that 2:4-dinitrodiphenylamine, on reduction by stannous chloride, only yields the amine under conditions which cause the azoxy-derivative to be formed in the case of all the other dinitro compounds examined. Similar observations in alkaline solutions had led Elbs to assume the following changes during the reduction of *o*- and *p*-nitroaniline and phenols:—



According to the views on substitution in aromatic compounds put forward by the present author, it seemed possible that, condensation to the azoxy-derivative being due to the residual affinity of the trivalent nitrogen in the hydroxylamine and nitroso-compounds, partial saturation of that residual affinity through the influence of an ortho- or para-amino- or hydroxyl group might prevent such condensation.

To decide this question, the behaviour of 2:4-dinitrodiphenylmethylamine was examined intramolecular change being here excluded. It was found that, in this case also, no azoxy-compound, but only the amine, is formed. Experimental evidence therefore favours the second of the above hypotheses.

*23. "The Relation between the Strength of Acids and Bases and the Quantitative Distribution of Affinity in the Molecule." By BERNARD FLÜRSCHHEIM.

It has been frequently observed that introduction of acidic or basic radicles into the molecule of an acid does not necessarily affect the dissociation constant in the expected sense, but often in the opposite direction. The author suggests the following hypothesis in explanation of this:—The dissociation constant of an acid is inversely proportional to the strength of the bond between the acidic radicle and hydrogen, and directly proportional to the strength of the linking between the acidic radicle and the negative electron. The latter depends on the more or less negative nature of the acidic radicle; the former, however, is chiefly a function of the amount of affinity which the atom to which hydrogen is linked can place at the hydrogen's disposal. This amount is variable, and its order of magnitude can in each particular case be foreseen by the application of general views previously advanced by the author.

Similarly, quaternary ammonium hydroxides and

analogous derivatives of oxygen, sulphur, iodine, &c., even when negatively substituted, may be strong electrolytes, because quivalent nitrogen can only weakly attract the hydroxyl group. Lastly, the salts of amines, &c., with acids are hydrolysed more readily when the nitrogen is linked to unsaturated atoms which absorb much of its affinity. A consideration of many affinity constants, hitherto thought abnormal, confirms these views, which have also been experimentally supported by the discovery that, when the basic group $\cdot\text{NMePh}$ is introduced in the ortho-position with respect to the amino-group of *m*-nitroaniline, the basicity of the latter is very considerably reduced.

*24. "Note on the Determination of the Rate of Chemical Change by Measurement of the Gases Evolved." By FRANCIS EDWARD EVERARD LAMPOUGH.

In a criticism of the author's work on this subject, J. C. Cain and F. Nicoll (*Proc.*, 1908, xxiv., 282) have contended that the solutions of diazobenzene chloride, the rate of decomposition of which was being determined by them from the rate of evolution of nitrogen, did not become supersaturated by the gas, and that no error was thereby introduced into their results.

With regard to the statements of Cain and Nicoll, it is manifest that their treatment of the solution (shaking, &c.) before measurement could not possibly prevent supersaturation occurring whilst measurement was taking place. Secondly, the ultimate evolution of the calculated volume of gas from the solution is merely evidence that the condition of supersaturation is only a temporary one. This would be expected of a metastable state, and is fully shown to be the case from the author's experiments.

A very simple direct experiment is, however, the most convincing proof that their reasoning is inadmissible. If a solution of diazobenzene chloride, prepared in the usual manner and rapidly heated with or without shaking, say, to 50°, is allowed to stand for ten or fifteen minutes, and the flask then gently revolved so as to set the liquid in fairly rapid rotation, a copious effervescence will at once be seen to result. The effect is still more clearly shown if the flask is connected to a pneumatic trough, in which case the liquid may be well agitated by shaking.

Experiments were made by the author which showed that under conditions of efficient stirring no acceleration of the reaction was produced by "colloidal" platinum. This is not surprising in view of the immediate precipitation of the metal from the colloidal state in the presence of the strong electrolytes contained in the solution.

In throwing doubt on the measurement of temperature, Cain and Nicoll appear entirely to have overlooked the experiment (*Proc. Camb. Phil. Soc.*, 1908, xiv., 590) by which it is proved that, throughout the time of measurement, the temperature of the reacting liquid did not differ more than 0.1° from that of the water-bath. A few words of a sentence from the author's paper are quoted apart from the context by Cain and Nicoll, so that they produce an entirely incorrect impression as to the actual procedure.

Finally, no suggestion of errors in temperature measurements could possibly dispose of the obvious conclusions from the comparative experiments performed with and without stirring at the same temperature and in the presence of the same platinum stirrer. In the experiments with agitation of the solution, the gas was at first evolved with high velocity, and this rate gradually diminished, strictly following the unimolecular law. In those without agitation, the rate of evolution was at first slow, gradually increased to a maximum value, and then diminished; if the stirrer was set in motion at any time in such an experiment, the immediate evolution of the large quantity of stored-up gas indicated a degree of supersaturation up to 100 times the volume normally dissolved. Again, in the experiments with stirring, the values of the velocity constant from first to last showed only very slight and irregularly-distributed differences from the mean value; in the experiments without stirring, and in those of Cain and

Nicoll, at best only a limited range from the middle of the experiment could be selected over which the calculated values of the "constant" (much lower than those of the experiments with stirring) might be plausibly uniform.

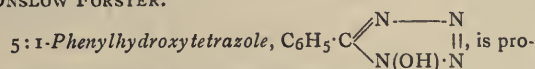
DISCUSSION.

Dr. VELEY remarked, with reference to the author's statement as to the rate of decomposition of oxalic by sulphuric acid, that it appeared unreasonable, if not romantic, to criticise work which he, the speaker, had never done, and conclusions at which he had never arrived.

From calculations made in a number of cases in which a gas is evolved from a solution by a process of chemical change, it appeared that the author had very greatly over-estimated the supersaturation value as at 100, or even more; it probably did not exceed 8 to 12, according to the nature of the gas and conditions of experiment.

Mr. LAMPLOUGH, in reply, pointed out that Euler performed his one comparison experiment with and without stirring at 25°. At this temperature the velocity of the reaction would be 100 times less, and the solubility of nitrogen only twice greater, than at the temperature of his (the speaker's) comparison experiment then under consideration, and a much closer agreement would therefore be expected. The author had hitherto confined his attention to the benzenediazonium compounds, and these had been investigated at temperatures from 36° to 67°. Mr. Lamplough offered apologies to Dr. Veley for the incorrect statement that he (Dr. Veley) had shown the decomposition of oxalic acid by sulphuric acid to be bimolecular. It should rather have been said that Dr. Veley found that the decomposition of formic acid by sulphuric acid was bimolecular, but had arrived at no conclusion from his experiments with oxalic acid (*Phil. Trans.*, 1888, clxxviii, 280, 291). Both these actions had since been shown to be unimolecular, the former by the author, the latter by Lichty, of Heidelberg, by a titration method. He further pointed out that his method of determining the degree of supersaturation was not theoretical, but practical, and confirmed his assertion as to the high degrees of supersaturation obtained by showing from the curves of an actual experiment that 37 cc. of solution at 62° held at one time 21 cc. of gas, which from the value 0.006 for the solubility of nitrogen at 62° represented a degree of supersaturation of more than 90. In justification of the words "plausibly uniform," an example was taken from Cain and Nicoll's paper (*Trans.*, 1902, lxxxi, 1416), from which it was shown that over a range of 15 per cent of the reaction there was a continuous variation of the velocity constant amounting to 12.2 per cent of its mean value, and the other experiment at the same temperature did not show a much greater constancy. He had, however, no intention of disputing that Cain and Nicoll had been able, owing to the very slight solubility of nitrogen, to show that the decomposition of diazobenzene chloride was possibly, even probably, a unimolecular action, but contended that the temporary state of supersaturation had seriously affected the values of their constants; in the case of actions which evolved more soluble gases, even the order of the reaction became untrustworthy. The crucial test of the development of this state was experiment, such as the simple one described above.

*25. "The Triazo-group. Part VII. Interaction of Benzhydroxamic Chloride and Sodium Azide." By MARTIN ONSLOW FORSTER.



duced, instead of the expected benzhydroxamic azoimide, when sodium azide and benzhydroxamic chloride interact; it melts and decomposes at 124°, undergoing spontaneous decomposition in the course of a few days, and is resolved by alkalis into benzonitrile, nitrogen, and nitrous oxide. The benzoyl, *p*-toluenesulphonic, and β -naphthalene-

sulphonic derivatives are stable, however, decomposing at 127°, 91—92°, and 101° respectively.

*26. "The Triazo-group. Part VIII. Azoimides of the Monobasic Aliphatic Acids." By MARTIN ONSLOW FORSTER and ROBERT MÜLLER.

A description was given of α -triazobutyric, α -triazoisobutyric, and α -triazoisovaleric acids, their amides and ethyl esters, with further information concerning triazoacetic and α -triazopropionic acids, these compounds having been studied with the object of determining the influence of environment on the stability of the triazo-group in the series.

*27. "Nitro-derivatives of Ortho-xylene." By ARTHUR WILLIAM CROSSLEY and NORA RENOUF.

In continuance of the work, briefly described in a preliminary note (*Proc.*, 1908, xxiv, 58), the action of nitrating agents on *o*-xylene has now been thoroughly investigated, with the result that all the theoretically possible mono-, di-, and tri-nitro-*o*-xylenes have been prepared. The methods adopted in establishing the constitutions of the various nitro-*o*-xylenes were discussed.

*28. "The Divergence of the Atomic Weights of the Lighter Elements from Whole Numbers." By ALFRED CHARLES GLYN EGERTON.

The atomic weights of the first fifteen elements have been calculated according to a simple formula, in which a constant is multiplied by a constantly increasing whole number in order to obtain the divergence from whole numbers of the atomic weights. The atomic weights of the next thirteen elements have been calculated according to a slightly modified formula. The agreement is, in nearly all cases, to the second place of decimals. The relation suggests a modification of Prout's hypothesis.

DISCUSSION.

The PRESIDENT said that he considered this as an epoch-making paper. The plan brought forward differed from all previous attempts to introduce regularly into the irregular series of numbers in the periodic table, inasmuch as it was based on a definite physical conception: the addition or subtraction of groups of electrons from the atoms; or, what came to much the same thing, definite amounts of electro-magnetic attraction which might conceivably alter mass.

*29. "The Constituents of the Bark of *Prunus serotina*. Isolation of *l*-Mandelonitrile Glucoside." By FREDERICK BELDING POWER and CHARLES WATSON MOORE.

The material employed, consisting of the air-dried bark of *Prunus serotina*, Ehrhart, yielded on maceration with water an amount of hydrogen cyanide corresponding with about 0.075 per cent of its weight. It has been shown to contain *l*-mandelonitrile glucoside, $\text{C}_{14}\text{H}_{17}\text{O}_6\text{N}$ (m. p. 145—147°; $[\alpha]_D^{20} 29.6^\circ$), which has also been obtained in the form of its tetra-acetyl derivative (m. p. 136—137°; $[\alpha]_D^{20} -24.0^\circ$), and an enzyme which hydrolyses β -glucosides. An alcoholic extract of the bark, on distillation with steam, yielded small amounts of benzoic acid and an essential oil, but no hydrogen cyanide. The non-volatile constituents of the bark consisted of a green resin, insoluble in either hot or cold water; a brown resin, soluble in the hot aqueous liquid, but deposited on cooling; and material which remained dissolved in the cold aqueous liquid. The green resin, amounting to about one per cent of the weight of the bark, yielded a phytosterol, $\text{C}_{27}\text{H}_{46}\text{O}$ (m. p. 135—136°; $[\alpha]_D^{20} -34.0^\circ$), palmitic, stearic, oleic, linolic, and isolinolenic acids, a little ipuranol, $\text{C}_{23}\text{H}_{38}\text{O}_2(\text{OH})_2$, and, after acid hydrolysis, oleic acid, dextrose, and β -methylasculetin, $\text{C}_{10}\text{H}_{18}\text{O}_4$. The brown resin, amounting to about one per cent of the weight of the bark, yielded, after acid hydrolysis, traces of a phytosterol, small amounts of oleic acid, β -methylasculetin, and dextrose, together with insoluble, red, resinous material. The portion of the alcoholic extract which was soluble in cold water contained the *l*-mandelonitrile glucoside, together with a quantity of sugar and tannin. It yielded,

furthermore, benzoic, trimethylgallic, and *p*-cumaric acids, traces of a substance melting at 240–241°, and, after heating with dilute sulphuric acid, *l*-mandelic acid and β -methylascutlein were obtained.

30. "*Benzyl and Ethyl Derivatives of Silicon Tetrachloride.*" By GEOFFREY MARTIN and FREDERIC STANLEY KIPPING.

The authors have made a study of certain benzyl- and ethyl-silicon compounds with the object of comparing their chemical behaviour with that of corresponding carbon compounds.

Tribenzylsilicon chloride and benzylsilicon trichloride, prepared by an improved method of applying the Grignard reagent, were decomposed by water, *tribenzylsilicol*, $\text{Si}(\text{CH}_2\text{C}_6\text{H}_5)_3\text{OH}$, and *benzylmetasilicic acid*, $\text{C}_6\text{H}_5\text{CH}_2\text{SiO}\cdot\text{OH}$, respectively being obtained. The former when boiled with concentrated hydrochloric acid or with dilute aqueous potassium hydroxide is converted into *tribenzylsilicic oxide*, $[(\text{C}_6\text{H}_5\text{CH}_2)_3\text{Si}]_2\text{O}$, a change not brought about by heating the silicol alone or with acetic anhydride; acetic chloride and benzoic chloride convert the silicol into the corresponding chloride. *Tribenzylsilicic oxide* is a colourless solid, m. p. 205°, soluble in chloroform, but sparingly so in light petroleum or alcohol.

Benzylmetasilicic acid, a resinous substance soluble in ether, does not exhibit properties analogous to those of a carboxylic acid; although soluble in potassium hydroxide solution, it does not form stable salts with organic bases. Its *ortho*-ester, $\text{C}_6\text{H}_5\text{CH}_2\text{Si}(\text{OEt})_3$, and the *oxide*, $[\text{C}_6\text{H}_5\text{CH}_2\text{Si}(\text{OEt})_2]_2\text{O}$, were prepared by treating benzylsilicon trichloride with ethyl alcohol; both are oils, boiling at 170–175°/(70 mm.) and 256–260°/(75 mm.) respectively. Attempts to prepare derivatives of silicon hexachloride by heating tribenzylsilicic chloride, benzylsilicic trichloride, and benzylethylpropylsilicic chloride respectively with sodium or potassium were unsuccessful.

Diethylsilicon dichloride was prepared from silicon tetrachloride by the Grignard reaction, but the yield was very poor; under certain conditions a considerable proportion of the tetrachloride gives non-volatile products, from which, after treatment with water, a yellow powder may be obtained; this substance is soluble in alkali hydroxides with evolution of hydrogen, but insoluble in all other ordinary solvents, and seems to have the composition $\text{C}_2\text{H}_8\text{O}_8\text{Si}_2$.

Diethylsilicon dichloride is decomposed by water, giving a polymerised oily *silicone*, $(\text{SiEt}_2\text{O})_n$; the hydrol, $\text{SiEt}_2(\text{OH})_2$, apparently is not formed.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, January 22nd, 1906.

Dr. C. CHREE, F.R.S., President, in the Chair.

MESSRS. A. Bannister, H. Bunsell, F. P. Fuller, T. Harris, and N. Willings were elected Fellows of the Society. Messrs. G. Nelson, W. F. Higgins, and D. Orson-Wood were admitted as Student Members.

A paper on the "*Effective Resistance and Inductance of a Concentric Main, and Methods of Computing the Ber and Bei and Allied Functions,*" was read by Dr. ALEXANDER RUSSELL.

The author gives the solution of the problem in terms of Kelvin's *ber* and *bei* functions and of two analogous functions which he calls *ker* and *kei* functions. The formulæ given previously by Maxwell, Rayleigh, Heaviside, Kelvin, and Sir Joseph Thomson are shown to be particular cases of his solution. Simple formulæ for calculating the functions used are obtained and are employed to correct errors in the tables given by Kelvin and also by Mascart and Joubert. The following simple formula for the effective resistance *R*, per centimetre length, of the inner

conductor of a concentric main for high frequency currents is obtained:—

$$R = (\rho m / 2\pi a) (0.7071 + 1/2ma + 0.265/m^2a^2 - 0.35/m^4a^4);$$

where ρ is the volume resistivity of the conductor, a its radius, $m^2 = 8\pi^2\mu f/\rho$, μ the permeability of the conductor, and f the frequency of the alternating current. This formula may be used in wireless telegraphy for calculating the resistance of a conductor when other conductors carrying high-frequency currents are not too close. For values of ma greater than 6 the maximum inaccuracy of the formula is less than 1 in 10,000.

In obtaining the solution, exact formulæ are obtained for the density of the current at all points on the inner and outer conductors.

The case of a concentric main with a hollow inner conductor is also considered. The method of obtaining the complete solution is explained, and approximate formulæ suitable for power transmission cables are given and numerical examples worked out. The approximate formula for the effective resistance at low frequencies, the proof of which is very laborious, has been previously obtained by Oliver Heaviside, and the author's solution is an independent verification of its accuracy. For high frequencies the formulæ become much simpler, and for very high frequencies the ordinary well-known formulæ are obtained. The formulæ given enable us to find the impedance of a concentric main, taking into account the variation of the current-density over the cross section of both conductors and the distributed capacity.

Mr. W. DUDELL congratulated the author, and remarked that the results obtained in the paper would be most useful. It was, he said, customary in dealing with high-frequency currents to use several parallel insulated wires instead of a single wire in order to increase the surface and obtain greater conductivity. He asked the author to what extent it was advisable to do this. He also asked how far it was valuable to silver-plate copper wires for high-frequency currents.

Mr. A. CAMPBELL observed with regard to Dr. Russell's warning that inductance standards might be greatly dependent on frequency, that well designed single-layer wavemeter coils of highly stranded wire (*e.g.*, 7/36") did not show according to his experiments a variation of more than 1 or 2 in 1000 in their self-inductance for frequencies from 0 up to 1,000,000 vibrations per second, the actual inductances being from 10 to 200 microhenries.

Dr. W. H. ECCLES remarked that in high-frequency work the resistance of a conductor depended on the nature of the surface. If a copper wire tarnished its resistance altered. Uniform results could be obtained by lacquering the wires. He congratulated the author upon the mathematical results obtained.

Mr. B. S. COHEN said that a knowledge of the variations with frequency of effective resistance and inductance of copper conductors was of considerable importance in connexion with telephonic transmission, and it was to be hoped that Dr. Russell would extend his valuable investigations to conductors lying side by side. The heaviest gauge of conductors met with in general telephonic practice is 2.85 mm. in diameter in the case of cables, and these conductors are separated by about 2.5 mm. of combined paper and air dielectric and twisted together with a lay of about 15 cm.

In the case of overhead open wires, the largest conductor in general use is 4 mm. in diameter, although in a number of cases a 5.69 mm. conductor has been used. The mean axial distance apart of these conductors is about 35 cm. as they are rotated in sets of 4 in a foot square.

Applying Lord Rayleigh's formula for effective resistance in these cases we get, for a frequency of 1500 vibrations, an increase of 1 per cent in effective resistance over steady current resistance in the case of the 2.85 mm. cable wire. A frequency of 1500 vibrations can quite safely be taken as the maximum frequency which is of any importance in speech articulation. The increase with the 5.69 mm. open

wire at this same frequency is 12 per cent, and with the 4 mm. wire it is 3.55 per cent. In a table given in a well-known Pocket Book, a 5.69 mm. conductor is stated to increase 15 per cent in effective resistance at 1500 vibrations, and he noticed that this figure had been adopted by one writer on telephonic matters. Mr. G. M. B. Shepherd some time ago worked out the decrease in inductance with frequency for wires lying side by side by both Heaviside's and Rayleigh's formulæ. The following percentage variations between 0 and 1500 vibrations were found for 5.69 mm. wire:— L 0.37 per cent decrease; r 0.22 per cent increase. This is very small, and is due to the fact that most of the inductance is due to the field between wire and wire. On the other hand, increase of resistance in this wire at 1500 vibrations means an increase in attenuation of 12 per cent.

In the case of 5.59 mm. conductors 33 cm. apart, the inductance as calculated by Maxwell's formula amounts to 3.2 millihenries, which would reduce the attenuation constant to one-fifth of its value at 1500 vibrations. It is very desirable, therefore, to know the order of decrease of inductance with frequency.

Lastly, I should like to ask Dr. Russell whether he thinks that the presence of the adjacent conductors in a telephone cable or open wire route is likely to modify the skin effect to any decided extent.

Mr. PATERSON expressed his interest in the paper, and asked if the formula given for the effective resistance of the core of a concentric main would be of the same form if the outer layer were removed. He also asked if the skin effect in the outer shell would be altered if the shell were cut parallel to its length and laid flat.

Prof. C. H. LEES pointed out that a change of sign in one of the early equations would lead to the use of the Bessel J function instead of the I function.

Dr. DRYSDALE congratulated the author, and wished to make a suggestion from the point of view of facilitating the use of these and other calculations. Electrical measurements frequently necessitated the employment of higher functions, and this involved either troublesome calculations or the compilation of bulky tables. He had therefore been led to try whether graphical methods could not be employed. The plotting of a function $f(x)$ graphically could only give values to a low degree of accuracy, but if some simple empirical formula $y = \phi(x)$ were found which approximated to the required function, it was possible to express the true value $f(x)$ in the form $r\phi(x)$ or $\phi(x) + a$, where r or a might be termed a correcting factor or term, which only varied between comparatively narrow limits. By employing a curve in which $\log r$ or a was plotted against x , it was frequently possible to obtain values of a function from a single curve correct to 1 in 10,000 or closer, and which greatly assisted interpolation. He had found this of great service in dealing with elliptic integrals and solid angles, and thought that it might perhaps also be applied to the ber and bei functions.

The AUTHOR, in reply to Mr. Duddell, stated that in his opinion stranding and insulating the strands of the wires used in wireless telegraphy would not diminish the skin effect, if the strands were parallel to the axis of the wire. It would probably increase it. Silver-plating the wires would be beneficial. The distribution of the high-frequency current on the surface of the wires can sometimes be found by remembering that the distribution is such that no magnetic induction is produced in the metal. The corresponding electrostatic problems are consequently of great help. Mr. Campbell's experimental results were interesting as they show that it is possible to make coils of low time constant so that frequencies even as high as a million have little effect on their inductance. These coils, however, are of little use for many experimental purposes. With ordinary laboratory coils a frequency of 10,000 will alter their inductance 2 or 3 per cent. If we have two parallel cylindrical wires practically touching, the inductance will alter from 3.7726 cm. per unit length to practically zero as the frequency is increased.

Dr. Eccles rightly lays stress on the importance of keeping the surface of the wires used in wireless telegraphy in good condition and careful lacquering would be very beneficial. Mr. Cohen's data about the telephone cables used in long distance transmissions are most interesting. A piece of metal adjacent to the wire would in many cases modify the skin effect, but it would be difficult to deduce any general rule as the main current is affected in different ways by the induced eddy-currents in the neighbouring metal according to the relative positions and magnitudes of the metal and wire. Mr. Paterson's question was rather hard to answer. In the hollow tube the current-density was a maximum at the outer surface. When split open and laid out flat, the current-density would be a maximum at the edges. In both cases, the uneven distribution of the current leads to an increase in the apparent resistance. But which would be the greater he could only determine by calculation. In reply to Professor Lees, he stated that he had first given the Kelvin functions in terms of Bessel's J function, but he had changed it to the I function as this made a + instead of a - in the fundamental definition. Dr. Drysdale's methods of calculation would be convenient in the case of the elliptic functions, but it would not be so easy to apply them to periodic functions of continuously increasing amplitude.

A paper entitled "*Note on the Luminous Efficiency of a Black Body*" was read by Dr. C. V. DRYSDALE.

The importance of efficient methods of light production renders it of interest to ascertain the possibilities of a black body as a light radiator at various temperatures, and the writer has attempted to obtain these from the radiation formula of Wien. The energy radiated between any two wave-lengths is written down and the total radiation calculated. This in conjunction with Kurlbaum's determination of the radiation constant, and Lummer and Pringsheim's results give rise to the formulæ given in the paper. A table and curves calculated from these formulæ have been worked out by Mr. A. F. Burgess, B.Sc., and show the relation of the total and luminous radiation and luminous efficiency for various temperatures. The comparison of the luminous energy so calculated with the intensity of light radiation found by Prof. Féry leads to a mechanical equivalent of light of about 0.75 watt per candle, which is a fairly probable figure. The results show the enormous extent to which the luminous efficiency is dependent upon the temperature and how extremely low it is at ordinary temperatures. At 1500° C. the efficiency is only of the order of 1 per cent, or less, while at 2000° C. it is about 3 per cent. The highest efficiency is obtained at a temperature of about 6500° C., and is then only between 40 and 50 per cent. This strongly points to the necessity for working in the direction of selective radiation or luminescence.

The SECRETARY asked the author if he could state exactly what he meant by the term "luminous efficiency." The ratio of luminosity to energy radiated was different in different parts of the spectrum.

Dr. RUSSELL thought that the physiological effect on the eye ought to be considered. If the paper had been entitled "The radiation efficiency, for rays contained within the limits of the visible spectrum, of a black body" it would perhaps have been described better. The sensibility of the eye to light rays varied not only with the wave-length but also with the intensity of the rays and the time during which they had been acting on the retina. If we only consider the objective stimulus of the luminosity, the author's implied definition might be, he thought, accepted. But if we consider, as we ought, that the subjective sensation produced in the normal eye has to be taken into account when judging luminous efficiency, another definition is required and the problem becomes far more complicated.

The AUTHOR, in reply, said that the term "luminous efficiency" was not very generally understood. There were three modes of defining it, of which two were due to Prof. Nichols, of Cornell University, who distinguished

between "total efficiency" and "radiant efficiency." The former of these quantities was the ratio of the luminous energy radiated between the spectral limits to the total energy consumption of the source of light, and the latter the ratio of the luminous energy as above to the total radiation from the source. As had just been pointed out, however, neither of these definitions took any cognizance of the very different luminosities of the various spectral colours, and this had been realised by Dr. C. Guilleaume, who had proposed to correct the luminous radiation by multiplying each ordinate of the radiation curve by a factor depending on the luminosity at that ordinate, which was unity at the point of maximum effectiveness (0.54μ). The author had proposed (*Proc. Roy. Soc.*, 1908) the term "reduced" total or radiant efficiency, for the efficiency expressed on this basis, and this was evidently the most rational one. The term "radiant luminous efficiency" was, however, recognised and had been correctly employed in the paper.

A paper on "*The Use of the Potentiometer on Alternate Current Circuits*," was read by Dr. C. V. DRYSDALE.

The great difficulty in alternate current measurement lies in the shortness of the range of the instruments available, and there is therefore a great need for some instrument which, like the direct potentiometer, should be capable of measuring P.D.s and currents of any range with accuracy. Two methods of attempting to apply the potentiometer principle to alternate current measurements seem possible:—(a) The balancing of the alternate current P.D. against a continuous P.D. with the assistance of some suitable balancing device, or (b) the balancing of two alternate current P.D.s. against one another. Suggestions or attempts at potentiometers on the first principle have been made, but seem unlikely to be successful owing to the insensitiveness of square law instruments at low voltages. The second method presents difficulties in that the two P.D.s. to be compared must be identical in magnitude, phase, and frequency, and approximately so in wave-form. The author's recent experiments with a phase-shifting transformer have led him, however, to attempt to use it with a potentiometer, and the measurements are then made in the same manner as with an ordinary direct current potentiometer, except that a vibration galvanometer or telephone is substituted for an ordinary galvanometer. By interposing an ammeter on the dynamometer principle in the main circuit of a potentiometer and deriving the current from the secondary of a phase-shifting transformer, it is possible to check the instrument with direct current against the standard cell in the ordinary way, and then to reproduce the same current in the potentiometer circuit and to bring it into coincidence of phase with the P.D. to be measured.

Experiments have been made with this device by Mr. A. C. JOLLEY and the author, first as to the accuracy of current measurement using an ordinary low-resistance standard, and have been found to give very good agreement with a Kelvin balance. Other tests have been made to obtain the vector difference of potential across a resistance coil and a choking-coil connected in series, and the triangle of voltages so formed was found to be very nearly closed. The tests so far made seem to indicate that an alternate current P.D. of 0.1 volt can be measured to an accuracy of 0.2 per cent or closer.

The author has also designed a universal potentiometer on this principle which serves both for direct and alternate current measurements, and for testing P.D., current, phase, power, inductance, capacity, &c.

Mr. A. CAMPBELL remarked that the first method suggested by the author had already been described by Mr. J. Swinburne (*Phys. Soc.*, Dec., 1893). It was also used with success at the Reichsanstalt in an improved form by Dr. DREWALL (*Zeit. Instrumentenkunde*, April, 1903). Dr. Drysdale's phase-turning method was interesting and would give good results in many cases. The vibration galvanometer, however, was so very much more sensitive

for its own frequency than for others, that it would not be likely to give any indication of errors due to other harmonics unless they were very pronounced. Hence the method must be used with great caution.

Mr. W. DUDELL expressed his interest in the paper, and asked if the limit of accuracy depended on the sensitiveness of the galvanometer, and if this was limited by the back E.M.F. of the instrument. He pointed out that the harmonics could be investigated by tuning up the galvanometer to be in unison with them. The device by which the phase was changed without changing the current was very useful.

Mr. RAYNER pointed out that the accuracy attainable depended on the sensitiveness of the Weston voltmeter employed. A vital point in the instrument was the phase-shifter with the sinusoidal windings. By using two galvanometers the fundamental and a harmonic could both be measured.

Mr. PATERSON, referring to the use of low resistances, said that errors might be introduced on account of their self-inductance. He thought that the discrepancies between the results given by the author's instrument and a Kelvin balance might be due to this rather than to inaccuracies of the balance.

The AUTHOR, in reply, said that he regretted that time had not permitted his making further investigations into previous work in this direction, but he had alluded to Mr. Swinburne's suggestions, and had claimed no credit for the electrostatic device. Mr. Campbell's criticisms mainly dealt with wave-form errors. Of course where iron cores at considerable saturation were employed, the distortion of wave-shape would be considerable, but with the single exception of power measurement which should then be made with a wattmeter, he knew of no object in such cases for accurate P.D. or current measurements. For ordinary standardisation of P.D. and current, this difficulty did not present itself, as there was no difficulty whatever in obtaining a sufficiently closely sinusoidal wave-form, and the wave-forms of the measured and balancing P.D.s. were usually similar, being derived from the same source. The use of a second vibration galvanometer tuned to the third harmonic would be excellent if it was desired to measure them, but he believed that it would rarely be necessary, and there should be no difficulty in making measurements to an accuracy of 0.1 per cent, with the ordinary alternators and resistances. For inductance and capacity measurements there was of course a positive advantage in an instrument which disregarded the harmonics. In reply to Mr. Duddell, there was no doubt that the vibration galvanometer did give a back E.M.F., as was shown by a telephone connected to its terminals when the coil was set in motion, and this would probably increase the damping, but he did not know the amount of the influence on the sensitiveness. He was glad the importance of the sinusoidal winding of the phase-shifting transformer was appreciated, and hoped that it would be found effective in preserving perfect equality of the potentiometer current as the phase was varied. It was true that slots or tunnels were employed in the stator core, but they were of considerable number, and the rotor and stator pitches were incommensurable. As to accuracy, it was true that this was limited by the dynamometer instrument, but this was fairly sensitive as it was always used at its best range, and it was to be doubted whether it was possible under any ordinary circumstances to make alternate current measurements to within an accuracy of a few parts in ten thousand, owing to variations in the alternator speed or E.M.F. Finally, he was certain that no ordinary low resistance standards would give any appreciable inductive errors. To produce an error in magnitude of 0.1 per cent would require a phase displacement of about 2.7 degrees, which was only slightly exceeded by helical iron wire resistances at 50 vibrations, and the straight strip resistances of the Reichsanstalt form were almost the perfection of non-inductive resistances. In any case inductance would not affect the closing of the vector triangle.

FARADAY SOCIETY.

Ordinary Meeting, February 9th, 1909.

Dr. V. H. VELEY, F.R.S., in the Chair.

Dr. S. RIDEAL, F.I.C., read a paper entitled "*Application of Electrolytic Chlorine to Sewage Purification and Deodorisation by the 'Oxychloride' Process.*"

This paper contains an account of an elaborate investigation carried out by the author at Guildford on the use of hypochloric solutions in sewage treatment. The experiments were made on a fairly large scale on the town sewage at the Corporation works. This when it emerges from the septic tank is dark coloured, more or less fetid from the presence of sulphuretted hydrogen, and contains very large numbers of bacteria, some of which are capable of producing disease. By adding a small quantity of a chlorinous liquid the odour is removed, and any nuisance arising from sewage distribution is completely avoided. But the most important feature is that the effluent is rendered harmless, the disease-producing organisms being destroyed. After the publication of the author's first experiments in 1904, the Royal Commission on Sewage Disposal visited Guildford and confirmed the results, further finding that the chlorine treatment did not hinder the subsequent purification in the bacterial coke filters. During 1907 and 1908 Dr. Rideal has continued the trials, and finds that the process actually *aids* the purification, first, by causing the filter-beds to mature more rapidly; secondly, by keeping the pipes free from fungus growths; thirdly, by the fact that the avoidance of clogging enables a finer filtering medium to be used, which gives better final effluents. The form of chlorine used was a hypochlorite solution prepared electrolytically. This method of sewage treatment has a great sphere of usefulness in preventing the pollution of rivers and in entirely removing aerial nuisance.

Mr. W. POLLARD DIGBY hoped that further information might be forthcoming concerning some of the more purely electro-chemical details of the "oxychloride" process, such as the construction of the diaphragms, strengths of solutions, salt consumption, costs, &c. He himself had found double diaphragms of considerable advantage. He emphasised the author's remarks on the importance of sewage sterilisation.

Mr. SHENTON pointed out that difficulties were likely to arise when storm waters vastly increased the volume of water to be sterilised, although this, of course, was only occasional. He thought that the prejudice many sanitary engineers felt against sterilisation would gradually disappear when it was realised how economical and practical many of the processes really were. Not sufficient was generally known about sterilisation.

Mr. MARTIN considered the storm difficulty more formidable than the last speaker had thought; to deal with twenty to fifty times the dry-weather flow required an enormous plant that must be ready to operate at any instant. The effect of chlorine in preventing the clogging of heads of pipes was an important feature in its favour.

Mr. A. B. THOMSON said it was difficult to give definite figures for costs, as these depended upon local charges for power and materials. He could not agree with Mr. Digby that distributing hypochlorite in carboys could not pay, seeing that electrolytic chlorine was a far better purifying and sterilising agent than chloride of lime, and, moreover, left no lime in solution to clog filters and otherwise give trouble.

Mr. J. FIELDHOUSE said that an automatic valve regulating the flow of hypochlorite from special storage tanks was used to admit of the necessary amount of steriliser in time of storm.

Mr. F. E. POLLARD took exception to the use of the word "oxychloride," which gave a wrong idea as to the constitution of the fluid.

Dr. S. RIDEAL, in the course of his reply, referred to the uncertainty surrounding the constitution of the electrolytic

fluid. It was usually supposed to consist of hypochlorite, but he had recently found that chlorites were present— ClO_2 ions. No chlorate was formed in the cold, either with or without a diaphragm.

NOTICES OF BOOKS.

Principles of Sewage Treatment. By Professor Dr. DUNBAR. Translated by H. T. CALVERT, M.Sc., Ph.D., F.I.C. London: Charles Griffin and Company, Ltd. 1908.

A THOROUGH investigation of the characteristics and treatment of sewage is put before the reader of this book, which has been excellently translated from the German. The history of river pollution is first discussed in some detail, the state of affairs in England being treated quite as fully as that in Germany, and the fact that in England there are specially difficult circumstances to be combated which are not met with on the Continent is fully recognised. The second part of the book, in which the present position of sewage treatment is considered, is mainly practical, and the author shows an extensive knowledge of the most modern methods of removing suspended matter and putrescibility, while his acquaintance with the procedure of even comparatively small sewage works in England is remarkably complete. The question of the utility and cost of the various methods of purification is discussed in the last chapter; from an impartial consideration of the data he has collected and compared, the author has formed the opinion that frequently the artificial biological processes would be found cheaper than irrigation, especially when the towns in question have grown to a certain size. He further thinks there is no doubt about the superior efficacy of the biological methods, and unhesitatingly decides in favour of them. The book has no exact counterpart in English, and its translation will no doubt be justified by an enthusiastic reception by all interested in the problem of the disposal of sewage.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

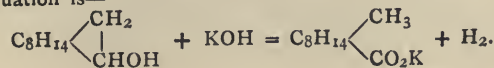
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences, Vol. cxlviii., No. 2, January 11, 1909.

General Method of Preparing Monoalkyl, Dialkyl, and Trialkyl Acetophenones.—A. Haller and Ed. Bauer.—The arylalkyl ketones of general formula $\text{C}_6\text{H}_5\text{CO}\cdot\text{R}$ in which R has the composition $\text{CH}_2\text{—R}^I$ and $\text{CH}\begin{smallmatrix} \text{R}^I \\ \text{R}^{II} \end{smallmatrix}$ (R^I and R^{II} being both aliphatic radicles), may be converted into di and trialkyl acetophenones of formula

$\text{C}_6\text{H}_5\text{COC}\begin{smallmatrix} \text{R}^I \\ \text{R}^{II} \end{smallmatrix}$ if they are dissolved in solvents such as ether or benzene hydrocarbons and subjected to the action of sodamide and alcoholic iodides. The authors have prepared by this method trimethyl, ethyldimethyl, methyl-diethyl, triethyl, methylethylpropyl, and allyldimethyl acetophenones.

Lævo-campholic Acid.—Marcel Guerbet.—A yield of about 75 per cent of l-campholic acid can be obtained by heating in sealed tubes l-borneol with caustic potash which has been recently dehydrated by fusion. The equation is—



The chemical properties of the lævo acid are similar to those of its dextro isomer. It is precipitated from alkaline solutions by carbon dioxide. Its ammonia salt dissociates very readily, and when the aqueous solution of this salt is evaporated at the ordinary temperature the ammonia volatilises and the acid is precipitated. Alcohols do not etherify it directly whatever the temperature, and to obtain ethers it is necessary to allow its anhydride or acid chloride to react with alcohols. Its ethers cannot be saponified by boiling with aqueous or alcoholic potash. Its anhydride, $(C_{10}H_{17}O)_2O$, may be prepared by dehydrating the acid with acetic anhydride. When boiled with absolute alcohol it is slowly transformed into ethyl campholate; when boiled with aqueous potash potassium campholate is formed; the reaction occurs more rapidly with alcoholic potash, but at the same time a little ethyl campholate is formed.

Alkaline Reduction of Orthonitrodiphenylmethane.—P. Carré.—Orthonitrodiphenylmethane, $C_6H_4(CH_2-C_6H_5)(NO_2)$, may be prepared by the condensation of orthonitrobenzyl chloride with benzene in presence of aluminium chloride and distillation in a current of superheated steam. It is best to rectify the raw product by distillation *in vacuo*. When it is dissolved in alcohol, boiled, and caustic soda and zinc dust are added, orthohydrazodiphenylmethane is formed and is deposited from the solution on cooling. With dilute acids this substance gives dibenzyl-2,2'-diamino-4,4'-diphenyl, $[-C_6H_3(CH_2-C_6H_5)(NH_2)_2]_2$. By reducing orthonitrodiphenylmethane with zinc and hydrochloric acid orthoaminodiphenylmethane can be prepared, and may be obtained in the crystalline state by distillation *in vacuo*.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xli., No. 18, 1908.

Determination of Cerium and other Rare Earths in Rocks.—M. Dittrich.—When oxalic acid or ammonium oxalate is added to a solution of a cerous salt, cerous oxalate is precipitated quantitatively. If a solution of a ferrous salt is added to that of the cerium salt a precipitate is still formed, but it contains iron. When some cc. of a neutral ferric salt are present no precipitate is obtained with ammonium oxalate or oxalic acid until they have been added in excess, when the red colour of the ferric salt is changed to the green of the complex ferric oxalate, and further addition of oxalate gives a pure white precipitate of cerous oxalate. Conversely, the oxalate precipitate is dissolved when a solution of an iron salt is added to it. Evidently the stronger ferric ions withdraw the oxalate residue from the cerous oxalate precipitate, forming complex ferric oxalate ions, and no precipitate can be formed until all the iron has been converted into the complex state. To separate the cerium quantitatively a very large excess must be used, 200 cc. of a saturated solution of ammonium oxalate for 0.2 gm. of cerous sulphate, and 15 cc. of concentrated ferric salt solution. It is better to use ammonium oxalate rather than oxalic acid, and to precipitate a hot solution. A dilute ammonium oxalate solution must be used for washing. In dealing with rocks it is best to remove silica by means of hydrofluoric acid and sulphuric acid, and to dissolve the residue in a little hydrochloric or nitric acid. On the addition of oxalate all the calcium is precipitated, and must be removed by igniting the precipitate obtained by adding ammonia to the residue after it has been dissolved in acid.

Products of Arc and Spark Discharge in Liquid Argon or Nitrogen.—Franz Fischer and George Ilivici.—Using electrodeless tubes the authors find that at gas pressures above 0.1 mm. the red argon lines disappear in presence of more than 4 per cent of nitrogen. Traces of nitrogen do not cause the disappearance of the argon spectrum with the authors' apparatus. Electrodeless tubes with different forms of outer covering were constructed,

and electrodeless comparison tubes with argon of density 19.94 (if the density of oxygen is taken as 16) were prepared with gas pressures of 3 mm., 0.3 mm., and 0.03 mm. of mercury. The silent electric discharge of pure hydrogen, argon, and a mixture of hydrogen and argon at the temperature of liquid air, in no case gave a change of volume, from which it could be concluded that a new molecule was formed. Experiments with titanium, tin, lead, antimony, and bismuth showed with certainty only the formation of nitrides; these may be due to traces of air in the apparatus. The nitrides of tin, lead, antimony, and bismuth on ignition *in vacuo* give up their nitrogen as N_2 , and yield ammonium salts with acids.

New Methods of Preparing Carbon Suboxide.—H. Staudinger and St. Bereza.—When oxides, for instance, silver oxide, act on malonyl chloride, or silver malonate or oxalate on malonyl chloride in the cold, the reaction takes place slowly, but in boiling acetic acid an energetic reaction takes place, and carbon suboxide is formed, but no ketene. The malonic acid anhydride first formed may split up, not into ketene and carbon dioxide, but into carbon suboxide and water, or, and this is the more probable supposition, the oxide splits the chlorine off from the malonyl chloride, and the suboxide is thus formed directly,

$$CH_2 < \begin{smallmatrix} COCl \\ COCl \end{smallmatrix} + Ag_2O = C \equiv \begin{smallmatrix} CO \\ CO \end{smallmatrix} + 2AgCl + H_2O.$$

NOTES AND QUERIES.

*. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Myrbane Oil—Can any reader inform me whether there is anything that may be added to myrbane oil to take away (or materially reduce) the very pungent smell without detracting from the property it possesses of removing paint stains and other marks from clothing, &c.
—R. G. L.

MEETINGS FOR THE WEEK.

- MONDAY, 22nd.—Royal Society of Arts, 8. (Cantor Lecture). "Modern Methods of Artificial Illumination," by Leon Gaster.
- TUESDAY, 23rd.—Royal Institution, 3. "Evolution of the Brain as an Organ of Mind," by Prof. F. W. Mott, F.R.S.
- WEDNESDAY, 24th.—Royal Society of Arts, 8. "Hand-made Papers of different Periods," by Clayton Beadle and H. P. Stevens.
- Society of Dyers and Colourists, 8. "Series of Azo-dyes derived from the Aminosulphonamides," by G. T. Morgan and Frances M. G. Micklethwaite.
- THURSDAY, 25th.—Royal Institution, 3. "Problems of Geographical Distribution in Mexico," by Hans Gadow, F.R.S.
- Royal Society of Arts, 4.30. "The Buddhist and Hindu Architecture of India," by A. A. Macdonell, M.A., &c.
- FRIDAY, 26th.—Royal Institution, 9. "Osmotic Phenomena, and their Modern Physical Interpretation," by Prof. H. L. Callendar, F.R.S., &c.
- Physical, 5. (At Finsbury Technical College, E.C., by invitation of Profs. Thompson and Coker). "A Laboratory Machine for applying Bending and Twisting Moments simultaneously," by Prof. Coker. "The Self-demagnetising Factor of Bar Magnets," by S. P. Thompson and E. W. Moss. Exhibition of Optical Properties of Combinations of Mica and Selenite Films (after Reusch and others) in convergent Polarised Light, by S. P. Thompson. Exhibition of - (a) Experiment to Illustrate the Temperature of Equal Density of Aniline and Water; (b) Simple Form of Thermo-electric Pyrometer for Students' Use; (c) Combined Metre-bridge and Potentiometer, with New Tapping-key Device, for Pyrometric and General Laboratory Work; (d) New Form of Carbon-plate Rheostat, suitable for Control of small Electric Furnaces, by C. R. Darling.
- SATURDAY, 27th.—Royal Institution, 3. "Properties of Matter," by Prof. Sir J. J. Thomson, F.R.S.

THE CHEMICAL NEWS

VOL XCIX., No. 2570.

SCANDIUM.*

PART I.—THE SEPARATION OF SCANDIUM FROM WOLFRAMITE FROM ZINNWALD.

By R. J. MEYER.

(Concluded from p. 87).

B.—Precipitation with Hydrofluoric Acid.

VERY little is known of the properties of the fluorides of the rare earths. It is only known that, with the exception of zirconium fluoride, they separate as difficultly soluble precipitates from neutral solutions of the salts. It has been shown that scandium fluoride is almost insoluble in a fairly strongly acid solution, a property which it shares with thorium fluoride, while the fluorides of the other earths are considerably more soluble in acids, but they can be almost completely precipitated if a large excess of hydrochloric acid is added to a solution of their salts. In order to prepare scandium in the pure state it is essential that the fluoride precipitate obtained from a solution rich in manganese and iron should be quite free from manganese, and that the accompanying cerium and yttrium earths should mostly remain in solution.

The oxide obtained after the concentration process with oxalic acid is dissolved in hydrochloric acid, the solution is evaporated to dryness on the water-bath, and the residue is taken up with water and some hydrochloric acid. The solution is placed in a lead dish, and hydrofluoric acid is added in the cold until the precipitate, which at first dissolves, remains; the whole is then heated for some time on the water-bath. The slimy precipitate then settles well, and it is best to aspirate it on a Nutsche filter into an oiled filter flask, and to wash with hot water. The precipitate consists of calcium fluoride, lead fluoride, a little iron fluoride, and the fluorides of the rare earths. It is then decomposed by concentrated sulphuric acid in a platinum dish; the solution is evaporated until a damp mass is obtained, and is then boiled with water. The calcium is removed by repeated precipitation with ammonia, and the hydroxides free from calcium are boiled with oxalic acid solution. In this way a finely crystallised oxalate is obtained, while the last traces of iron remain in the solution. The oxides obtained on ignition must be perfectly white. In different experiments the yield from 1 kilogram of wolframite was 1.4 to 1.6 grms. of oxide, and 3.0 to 3.3 grms. of oxide from 1 kilogram of technical wolframite oxides.

Owing to the success of the experiments with the fluoride purification, it seemed feasible to give up the preliminary concentration with oxalic acid and to precipitate the original solution at once with hydrofluoric acid. This was found to be perfectly satisfactory as long as only small quantities, i.e., about a kilogram., of wolframite oxides were being treated. With larger quantities it was difficult to get suitable vessels for the precipitation of large volumes of liquid with hydrofluoric acid; moreover, a very considerable amount of hydrofluoric acid is used, because the greater part of the aluminium, in which the solutions obtained from impure material are very rich, must be precipitated as fluoride in order to be sure of completely precipitating the rare earths. For this reason it is usually best to perform the preliminary concentration with oxalic acid.

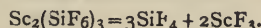
By this combination of methods 30 kilograms of wolframite oxides were worked up in several portions. The yield amounted to 75 grms. of a raw scandium containing always over 95 per cent of scandium oxide. As the oxides

on extraction with hydrochloric acid left 6 grms. of insoluble residue, the result corresponds to a yield of 0.25 per cent of the raw, and 0.29 per cent of the pure material.

(When smaller quantities were used the yield rose to 0.3 to 0.33 per cent of the raw material. The losses are due to the difficulty of treating such large quantities in a scientific laboratory).

C.—Methods with Hydrofluosilicic Acid.

The combined oxalate and fluoride method, as we have seen, gives good results, but certain definite instructions have to be very carefully followed; moreover, it is very tedious when large quantities of raw material have to be worked up. In addition, exceedingly large quantities of oxalic acid are absolutely necessary to precipitate the small quantities of the rare earths, and finally there are inconveniences attached to the use of hydrofluoric acid, due to its attack upon the apparatus, and also to its bad effects upon the health. It therefore seemed desirable to try to find a more convenient, less lengthy, and at the same time economical method. This was accomplished by replacing the hydrofluoric acid by hydrofluosilicic acid or sodium silicofluoride. It was first observed that the different groups of the rare earths behave very differently towards hydrofluosilicic acid. In neutral solution all rare earths are precipitated when hydrofluosilicic acid is added and they are boiled; on the other hand, in acid solution no precipitate is formed in solutions of the yttrium earths even on boiling, while with the cerium earths—cerium, lanthanum, praseodymium, neodymium, samarium—very striking differences are observed in their precipitability; I shall discuss these more fully later. Scandium, even in strongly acid solution, is gradually completely precipitated on boiling, and it is thus obtained quite free from foreign earths. These reactions merit a more thorough study, especially in relation to the possibility of successfully separating the rare earths with their help. The scandium is not precipitated as silicofluoride, but as fluoride, the silicofluor ions, SiF_6^{--} , being decomposed on boiling, yielding silicon fluoride and F^- ions:—



The yttrium earths are not precipitated under the same conditions, because with them the decomposition does not occur at any rate in acid solution. (Cerium earths are present only in very small quantities in wolframite; of them, neodymium and samarium show a certain tendency to be precipitated by hydrofluosilicic acid). This reaction was applied to the separation of scandium from the solution of wolframite oxides. It was found that in this case concentration by means of the oxalate could be omitted without any ill effects, for comparatively small quantities of hydrofluosilicic acid were sufficient to precipitate from a solution saturated with iron salts, the earth nearly free from iron and calcium and quite free from manganese and lead. As an acid reaction of the solution does not hinder the precipitation, the oxides can be dissolved in an excess of acid without subsequently neutralising or evaporating. The whole separation process is thus greatly simplified. Instead of aqueous hydrofluosilicic acid, commercial pure sodium silicofluoride may advantageously be used, the operation being carried out as follows:—One kilogram of the wolframite residues is dissolved in 3 litres of raw hydrochloric acid, the powder being introduced into the boiling acid. After drawing off the deposit of silica and boiling with dilute hydrochloric acid the filtrates are put together and boiled, and 40 grms. of solid sodium silicofluoride are added, meanwhile stirring the whole. The boiling is then continued for about half-an-hour, when the scandium fluoride separates completely in the form of a white pasty precipitate; it settles after standing for some time, and then the supernatant acid liquid, which contains iron, can be decanted off. The precipitate is then filtered on a Nutsche filter, and again boiled with very dilute hydrochloric acid (1 litre of water to 300 cc. of dilute hydrochloric acid). It is then perfectly colourless. As

* *Zeitschrift für Anorganische Chemie*, lx., 134, November 17, 1908.

described above, the fluoride is decomposed with sulphuric acid, the sulphate solution is precipitated with ammonia, and finally the hydroxides are decomposed with oxalic acid. When the oxalate thus obtained is ignited, a perfectly white scandium oxide, almost free from foreign matter, is obtained. As with the other methods the yield amounts to 3 to 3.3 grms. Sc_2O_3 from 1 kilogram. of wolframite oxides.

Composition of Oxides obtained by Methods A, B, and C.

The oxides obtained by the three above described methods of isolating scandium from wolframite oxides were investigated:—(1) By examining the spark spectrum; (2) by determining the atomic weight. The atomic weight was determined by Nilson by converting a known weight of the oxide into sulphate; *i.e.*, by finding the ratio of R_2O_3 to $\text{R}_2(\text{SO}_4)_3$. After various experiments in this direction it was found to be preferable to reverse the process; *i.e.*, to convert an unweighed amount of oxide into sulphate, and to change this again to oxide by strong ignition after weighing, for when the oxide is dissolved in acid and the sulphate solution is evaporated in a crucible losses very often occur owing to spitting; these losses, of course, do not matter if we start with sulphate. (Ignited scandium oxide does not dissolve completely in acids until it has been boiled for a long time). This method is also quicker. Moreover, in order to convert the oxide into sulphate, it is not necessary first to dissolve the former in hydrochloric or nitric acid and then add sulphuric acid to the solution as with the other rare earths; the scandium oxide can be dissolved directly by boiling with dilute sulphuric acid, as its sulphate is readily soluble. In order to get the neutral anhydrous sulphate, a temperature of 430–450° is required. This operation was carried out in a small electric resistance furnace. The temperature was measured with a Le Chatelier's pyrometer and a gauged millivoltmeter. In this way absolute constancy of weight could be obtained easily. The conversion into oxide was performed by igniting before the blowpipe. The results of some atomic weight determinations are given in the following table:—

No.	Method of separating oxide.	Weighted $\text{R}_2(\text{SO}_4)_3$.	Weighted R_2O_3 .	At. wt. R ^{wt.}
1.	Oxalic acid + hydrofluoric acid	2.9876	1.1419	50.2
2.	Oxalic acid + hydrofluoric acid	1.9989	0.7478	47.8
3.	Hydrofluoric acid alone ..	0.7392	0.2764	47.6
4.	Hydrofluosilicic acid ..	3.0800	1.1370	46.2
5.	Hydrofluosilicic acid ..	3.0678	1.1268	45.6
6.	Sodium silicofluoride ..	2.0329	0.7523	46.4

Appearance of Oxide.—No. 1, yellowish; Nos. 2 and 3, very faintly yellow; Nos. 4, 5, and 6, pure white.

As 44.1 has been taken for the atomic weight of scandium since Nilson's work was published, it follows that the "unfractionated" oxide obtained by the above described precipitation methods possesses a high degree of purity. This is specially the case with the preparations obtained by the hydrofluosilicic acid method, while the specimens prepared by precipitation with oxalic acid and hydrofluoric acid, or with hydrofluoric acid alone, are not so pure. Hence it follows that hydrofluosilicic acid in acid solution is a specific reagent for scandium, while oxalic acid precipitates all the earths which are present in the raw material, and hydrofluoric acid does not completely eliminate the accompanying cerium and yttrium earths; at any rate, the result with these reagents depends largely on the acidity of the solution and the amount of reagent added. In concentrated solution Specimen 1 (see above table) showed plainly the strongest absorption bands of erbium, and also the most intense neodymium bands in the yellow; it was obtained by precipitating the fluoride from an almost neutral solution with a large excess of hydrofluoric acid. In Specimens 2 and 3, which were prepared from acid solutions, the absorption bands could not be seen clearly, but according to Prof. Eberhard's communication the examination of the arc spectrogram of 2 showed the undoubted presence of cerium and yttrium

earths; the lines of yttrium and ytterbium in particular were plainly visible, while in Specimen 5 only traces of foreign earths could be detected. According to an approximate estimation even the relatively most impure specimen, No. 1, contains at least 93 to 95 per cent of scandium.

D.—Removal of the Foreign Earths by Precipitation with Sodium Thiosulphate.

According to the plan of this research all fractionation methods, which must of necessity waste the valuable material more or less, had to be avoided, and only precipitations could be employed. This scheme could be carried through owing to the peculiar nature of scandium. The spectrographic examination of raw scandium had shown that it still contains small quantities of yttrium earths. Sodium thiosulphate was found to be an excellent reagent for completely removing all foreign earths. Cleve had already observed that scandium is precipitated when boiled with thiosulphate, but he stated that the precipitation was incomplete. This restriction was undoubtedly based upon an error, and may probably be explained by the fact that Cleve's preparation contained some ytterbium. (As Prof. Eberhard points out, the spectrographic examination of Cleve's scandium shows the presence of a considerable amount of ytterbium; this also explains why Cleve's values for the atomic weight, 44.91 and 45.12, are too high). As a matter of fact, pure scandium is precipitated quantitatively from its neutral solution by the addition of thiosulphate at 100°; it separates in the form of a grey flaky precipitate, which consists of scandium thiosulphate—not the hydroxide. Other rare earths, except thorium, are not precipitated by this reagent. Thus, by a thiosulphate precipitation a yellow oxide of atomic weight 50 could be converted into a pure white oxide of atomic weight 45–46, the accompanying earths remaining dissolved in the filtrate. Even ytterbium, which is most persistently retained by scandium when the method of fractionally fusing the nitrates, used by Nilson and Cleve, is employed, may be removed in this way. (I obtained a specimen of chemically pure ytterbium oxide through the kindness of Dr. Urbain, of Paris). Thus it might be expected that chemically pure scandium could be obtained by this method. However, it was found that this process always gave a product the atomic weight of which was higher than 46. A raw scandium, obtained by precipitation with hydrofluosilicic acid, of atomic weight 46.2 (No. 4 in the above table), was divided into two fractions by sodium thiosulphate; a small amount of the foreign earth remained dissolved in the filtrate. The result of this experiment appeared remarkable at first sight, for it was found that the first fraction possessed a higher atomic weight than the original product.

Raw Earth, 46.2.

Thiosulphate pre- cipitate.	Weight of sulphate.	Weight of oxide.	Atomic weight.
Fraction I.	2.1985	0.9170	46.9
" II.	1.3610	0.5012	45.9

This experiment was repeated somewhat differently with a larger amount of scandium oxide; the result obtained was the same. Ten grms. of oxide of atomic weight 45.6 (No. 5 in the above table) were dissolved in hydrochloric acid; the neutral chloride solution was boiled and precipitated with the calculated amount of sodium thiosulphate necessary for complete precipitation (60 grms.). By precipitation of the filtrate with ammonia 0.1347 gm. = 1.34 per cent of a brownish mixture of earths, not precipitated with thiosulphate, could be isolated. The thiosulphate precipitate was decomposed with hydrochloric acid, and the solution was precipitated with oxalic acid after evaporation. The oxide obtained by igniting the oxalate had the atomic weight 46.4.

Raw Earth, 45.6; Thiosulphate Precipitation.

Weight of sulphate.	Weight of oxide.	Atomic weight.
1.9332	0.7148	46.4

This increase in the atomic weight in the thiosulphate precipitate could only be explained by supposing that it was due to the concentration of an earth of higher atomic weight also precipitated by sodium thiosulphate. This could only be thorium. Naturally the presence of this substance cannot be proved qualitatively with certainty, for at present no reaction has been discovered by which small quantities of thorium can be detected in presence of scandium. But in this case also the spectrographic examination gave a significant result. According to Prof. Eberhard, the earth obtained by precipitating with thiosulphate is quite free from cerium and yttrium earths, but in the arc spectrum it shows perfectly plainly the lines of thorium. On the probable assumption that thorium is the only impurity which is not separated from the scandium when thus purified, and that the atomic weight 44.1 given by Nilson is correct, the amount of thorium present may be calculated to be about 1 per cent. The presence of this impurity in scandium oxide was to be expected from the nature of the separation process adopted, if thorium was contained in the wolframite earths; for like scandium it would be completely precipitated in acid solution, both by hydrofluoric acid and by hydrofluosilicic acid.

As was to be foreseen, the removal of this last small impurity is very difficult, owing to the great similarity in the behaviour of scandium and thorium. Besides resembling thorium in being precipitated by hydrofluoric acid, hydrofluosilicic acid in acid solution, and by thiosulphate, scandium compounds like those of thorium, are readily soluble in alkali carbonates and alkali oxalates, and these solutions are precipitated on boiling with much water. Scandium is also precipitated to a certain extent by hydrogen peroxide in neutral solution. As for any differences in behaviour, these cannot be used for the separation of the very small quantities of thorium in question, as the experiments we have described have shown. The most striking differences are, for example, the behaviour of the strongly ignited oxides towards acids, in which thorium oxide is insoluble, while scandium oxide is soluble after prolonged boiling; also the very great difference in the solubilities of the oxalates of the two elements in acids, the well developed tendency of thorium salts to undergo hydrolysis, and finally the volatility of scandium chloride. There can be no doubt that the more thorough study of these and other distinguishing reactions would lead to the solution of the problem, and that it would then be possible to prepare scandium in a perfectly pure state without performing any fractionations whatever.* As in the course of new preparation processes performed on a large scale, I shall shortly obtain some hundreds of grms. of scandium oxide, I shall be able to proceed at once to a thorough study of this interesting element which has up to the present been so very seldom prepared. With the yields now obtained, 1 kilogram. of 98 or 99 per cent scandium oxide can be prepared from 330 kilograms of wolframite oxides, which can be prepared on a manufacturing scale without any difficulty.

The preparation of scandium from other raw materials, tin-stone and tin-slag, will be described in a second article. The experiments on the purification of the oxide will be continued. In addition, the scandium compounds will be thoroughly studied from a chemical and physical-chemical point of view, and the atomic weight will be re-determined.

I must not omit to express my hearty thanks to Herr Max Speter for the valuable assistance he gave me in discovering and working out the hydrofluosilicic acid method.

Summary.

1. Wolframite from Zinnwald contains 0.14 to 0.16 per cent of rare earths, including a considerable amount of scandium oxide. When the mineral is opened up with soda all the scandium goes into the oxides (iron, manganese, calcium, lead) separated from sodium tungstate by extrac-

tion with water. These raw wolframite oxides, which contain 0.30 to 0.33 per cent of scandium oxide, form the raw material for the preparation of scandium.

2. Two methods of separating scandium from the wolframite oxides were worked out.

- a. Precipitation with hydrofluoric acid from an intermediate product in which the scandium had been concentrated by an oxalic acid precipitation.
- b. Precipitation with hydrofluosilicic acid or sodium silicofluoride in acid solution.

NOTE.—The preparation of scandium by the combined oxalic acid, hydrofluoric acid method, has been patented by the author (D.R.P. 202523). The method with hydrofluosilicic acid is the subject of a specification which is now before the Royal Patent Office.

3. The raw scandium oxide prepared by the above methods still contains small quantities of foreign earths (yttrium earths, especially yttrium and ytterbium), particularly if method b has been used. These may be completely removed by precipitating the scandium with sodium thiosulphate.

4. The scandium when freed from cerium and yttrium earths has the atomic weight 45 to 46; it still contains about 1 per cent of thorium.

THE FRUIT OF MEDEOLA VIRGINICA AND AMPELOPSIS QUINQUEFOLIA.

By LOIS E. POYNEER and H. LEROY DUFFIN.

THE fruit of *Medeola Virginica* (Indian cucumber) was gathered at Sylvan Beach, New York, on the sandy shores of Oneida Lake, August 30 to September 6, 1907. Only about one-half of the fruit seemed ripe. We found it necessary to leave the locality early in September, otherwise the whole quantity would have been gathered when fully ripe. It was dried in an oven at about 105°. Each fruit averages about 0.05 gm. in weight. They are about the size of currants, dark brown, almost black in colour. There is on each a rather hard outer shell, and within this are six to twelve small nutlets which are very hard. These nutlets are dark coloured like the outside of the fruit.

The Sugars.

We placed 100 grms. of the fruits in a 500 cc. flask, with which was connected a back-flowing condenser. 300 cc. of alcohol was added. The flask and contents were kept on a warm water-bath for ten hours, and the alcoholic extract poured into a second flask, and the alcohol removed by distillation. The same alcohol could be used over and over again. This treatment was continued until all the sugar was removed, as shown by Fehling's solution. The time necessary was six weeks. Each separate portion of alcoholic extract was brown in colour, the intensity of the colour gradually diminishing. The residue in the flask after the alcohol had distilled over had an odour of black-berry brandy and burned apple butter.

To determine the amount of sugar, water was added to the residue from the alcohol, sufficient to make 350 cc. of solution, and 1 cm. was added to 50 cc. of distilled water. This was titrated with Fehling's solution, of which 10 cc. corresponded to 0.05 gm. sugar. This indicated 66.6 per cent of sugar, a figure which is probably too high. When yeast was added to a solution of the sugar it easily fermented, and was converted into alcohol.

A small quantity of the sugar solution was digested with purified bone-black, after which the solution was quite clear. Then we placed in a test-tube one-tenth gm. of the dried sugar, two-tenths gm. pure phenyl hydrazine, three-tenths gm. sodium acetate, and 2 cc. distilled water. On immersing this in a bath of boiling water the osazone began to appear in half a minute, and all seemed to have

* Experiments which were performed while this article was being printed have already indicated a method of removing thorium. This method will be described in a subsequent article. (Correction).

separated in one minute, indicating that the sugar is fructose. The osazone was filtered off and re-crystallised a number of times from alcohol, but we did not succeed in obtaining sufficient of the pure substance to determine the melting-point.

The Oils.

The portion of the fruit that remained after the alcoholic extraction was dried in an air-bath, and the husks separated by rubbing. We attempted to remove the husks by "panning" with water, but were unsuccessful, as some of the nutlets were also inclined to float away, and finally most of the husks were separated by gently blowing upon them.

The nutlets proved to be very hard. They could not be crushed with a heavy iron mortar and pestle, but by running them three times through a coffee grinder, set with a small aperture, they were ground moderately fine. They had an odour which reminded one of varnish.

The ground nutlets were treated with ether in a flask with an inverted condenser, as the fruits were first treated with alcohol.

53.2299 grms. of the dried nutlets gave 5.4770 grms. of oil. After standing in a test-tube there seemed to be two distinct oils. The top layer was removed with a capillary tube. It was quite light in colour. On standing in an open tube this evaporated during the night. The oils were again obtained from a second portion of berries, but the lighter portion was accidentally lost. On placing them in a freezing mixture, they did not solidify. A small portion of oil was extracted by the alcohol with the sugars. On treating this extract with ether, the oil was easily recovered and added to the main portion.

The heavier of the two oils, light in colour, attractive in appearance, and apparently pure, was saponified with a normal solution of caustic soda, and the saponification equivalent was found to be 254.88. This indicates that it belongs to the group of marine oleins. The low equivalent shows that it is not one of the waxes. According to Allen, the equivalent of porpoise oil is 256 to 260, and the specific gravity is 0.92. We found the specific gravity of our oil to be 0.935. It saponified with ease and formed considerable soap. These are likewise characteristics of porpoise oil.

After purifying the alcoholic extract with bone-black, it gave the test for oxalic acid, but no other acids were detected. When a berry held in platinum wire was inserted in the Bunsen flame, a decided reaction for potassium was noticeable.

The Ash.

We burned 3.7530 grms. of the fruit in a platinum dish, and obtained an ash weighing 0.1468 gm., or 3.91 per cent of the whole. The constituents were determined as follows:—

SiO ₂		18.00	per cent of the ash
Al ₂ O ₃		0.66	" "
Fe ₂ O ₃		2.65	" "
CaO		6.13	" "
MgO		8.04	" "
K ₂ O		24.50	" "
Na ₂ O		1.63	" "

The ash effervesced on treatment with hydrochloric acid, but neither the carbon dioxide nor the sulphate content was determined. The P₂O₅ was estimated from the residue after the alcohol and the ether extraction. We obtained from 2.2748 grms. of the dried residue, 0.1515 gm. of ash, or 5.26 per cent. It would naturally be expected that the percentage of ash would be higher than in the original fruit. We obtained a half mgrm. of P₂O₅, or 0.33 per cent of the ash.

The *Ampelopsis Quinquifolia*.

The *Ampelopsis quinquefolia* (Virginia Creeper, also called American Ivy) is a common woody vine, growing in

rich ground, climbing extensively, blossoming in July, ripening its small black berries in October, leaves turning bright crimson in autumn ("Gray's Manual").

The Sugars.

A quantity of the ripe blackish berries were picked from the vines on the Cornell College Campus, October 19, 1907. They were afterwards dried at 105°. The average weight was 0.116 gm.

We weighed out 150 grms. of the dried fruit in a 500 cc. flask, filled it three-fourths full of alcohol, attached an inverted condenser to the flask, and heated it on the water-bath. The alcohol was poured off, and a fresh portion added every six hours. This operation was continued several days until no more colouring matter was given from the fruit, and the extract gave no sugar test with Fehling's solution. The alcoholic extract was dark reddish brown in colour, and gave a decided acid reaction with litmus-paper. After all the alcohol was removed by distillation, sufficient water was added to the residue to make 350 cc. This, tested with Fehling's solution, was found to contain 91 grms. of sugar, or about 60 per cent of the original fruit.

A portion of the extract was treated for several days with purified bone-black, which removed most of the colouring matter. This sugar solution was next evaporated to dryness. We placed in a test 0.8 gm. phenyl hydrazine hydrochloride, 0.8 gm. of sodium acetate, and 0.2 gm. of the sugar, and dissolved in a little water. The solution was placed in a boiling water-bath, and the osazones appeared in one to one and a-half minutes, indicating fructose. After crystallising the precipitate from alcohol, the melting-point was found to be 204°.

The Acids.

The extract that had been purified with bone-black was shown to contain oxalic acid and tannic acid.

The Oils.

After extracting the fruits with alcohol, they were dried in an air-bath and ground to a fine powder. The oils were extracted with successive portions of ether, as the sugars had previously been extracted with alcohol. We obtained 16.5054 grms. of oil, equivalent to 11.27 per cent of the fruit. On standing, the oil soon separated into two distinct portions, one considerably darker than the other; the darker portion was also the heavier.

We saponified both portions separately with alcoholic caustic potash solution, but arrived at no satisfactory results. The darker oil easily solidified in a freezing mixture and afterwards melted at 0.8°. The specific gravity of the two portions shaken together was found to be 0.9503. The oils were probably palmitin and olein, probably on account of the high percentage of sugars. We received 0.0976 gm. of ash from 2 grms. of the crushed fruit, or 4.88 per cent. This analysed as follows:—

Silica		0.00	per cent of the ash
Fe ₂ O ₃		1.86	" "
Al ₂ O ₃		4.81	" "
CaO		42.27	" "
MgO		3.90	" "
K ₂ O		28.15	" "
Na ₂ O		3.97	" "
P ₂ O ₅		10.04	" "
SO ₃		5.00	" "

No test was made for nitrogen or proteids.

The fruit held in the Bunsen flame with a platinum wire gave a decided potassium reaction, both with and without the blue glass.

We desire to thank Prof. N. Knight for encouragement and assistance in carrying on the foregoing work.

Cornell College, February 6, 1909.

THE ATOMIC WEIGHT OF TELLURIUM.

By VICTOR LENHER.

THE atomic weight of tellurium has received an unusual amount of study ever since attention was directed to it by the statement of Mendeleeff in his memorable paper before the Russian Chemical Society in 1869. In outlining the principles of the periodicity of the elements he observed that "the atomic weight of tellurium must be between 123 and 126, and cannot be 128."

Various lines of experimentation have been followed to test the validity of this assertion:—(a) Critical studies have been on the elementary character of tellurium, but nothing thus far has developed which would warrant a belief in its complexity from the character of the experimental evidence produced. (b) The spark spectrum of the element has been studied, especially by K $\ddot{o}$ thner (*Ann.*, cccix., 1), who purified his material by various processes, and who used tellurium from various sources. His results show no differences in the spectrum. (c) Numerous atomic weight determinations have been published from time to time with tellurium from various sources, but the results of all the experiments seem to indicate that the figure is higher than that of iodine.

It is the purpose of this paper to describe a series of atomic weight determinations made with three specimens of tellurium from widely different sources, and by the use of a method different in principle from any previously used with tellurium.

The salt chosen for the work has been the double bromide of tellurium and potassium, K_2TeBr_6 , a salt readily obtained in a high degree of purity and one of the most strongly crystalline derivatives of tellurium. This salt when heated in a current of chlorine is converted into potassium chloride, tellurium tetrachloride, and bromine. The latter two substances, being volatile, are driven off, and the last trace of tellurium can be expelled from the potassium chloride by heating in a current of hydrochloric acid gas. In this method potassium tellurium bromide is originally weighed, and later potassium chloride. It is thus possible to obtain a tellurium figure through the ratios of bromine, chlorine, and potassium, and to eliminate the possibility of an error in the weighing of tellurium, which may contain oxygen when precipitated from solution and dried. It also does not require the formation of insoluble silver bromide by double decomposition with this salt, a reaction to be avoided if possible, inasmuch as the tellurous acid formed by dissolving the salt in water tends to form insoluble silver tellurite which would contaminate to a greater or less extent the silver bromide formed. By this method of weighing potassium tellurium bromide and subsequently weighing potassium chloride any question of the ratio of tellurium and oxygen would be removed.

Preparation of Material. Tellurium from Colorado.—Through the courtesy of Prof. C. W. Stoddart, a quantity of tellurium gold ore was obtained from the Clarissa Tunnel, Boulder County, Colorado. The ore is graphic tellurium containing about 3 per cent of gold and a little silver in a vein rock of quartz.

The ore was extracted with hot nitrohydrochloric acid, the extract was converted into hydrochloric acid solution free from nitric by repeated evaporation with hydrochloric acid, after which sodium acid sulphite was added, and the impure tellurium precipitated. The dried precipitate was fused with potassium cyanide in order to separate the heavy metals and to allow of the separation of the sulphur and selenium from the tellurium. After extraction with water and filtration from the gold and other heavy metals, a current of air was passed through the solution, and the tellurium precipitated, the sulphur and selenium remaining in the cyanide solution. One hundred grms. of tellurium thus obtained were precipitated from the chloride solution by means of sulphur dioxide gas, after which it was converted into basic nitrate. The re-crystallised basic nitrate was converted by ignition into the oxide.

		Atomic weight Te.	
		1.	2.
Weight K_2TeBr_6 .	Weight KCl.		
SERIES I.— <i>Tellurium from Bohemia.</i>			
2'33360	0'50779	127'31	127'54
1'27372	0'27716	127'32	127'54
1'47573	0'32111	127'33	127'56
1'65715	0'36059	127'33	127'55
1'54006	0'33513	127'29	127'51
Mean		127'32	127'54
SERIES II.— <i>Tellurium from Copper Ores.</i>			
1'82810	0'39778	127'34	127'56
1'87342	0'40765	127'33	127'55
1'48045	0'32214	127'33	127'55
2'24775	0'48911	127'31	127'54
Mean		127'33	127'55
SERIES III.— <i>Tellurium from Colorado.</i>			
2'37899	0'51767	127'31	127'54
1'79926	0'39146	127'41	127'64
0'94102	0'20476	127'33	127'56
1'55357	0'33806	127'31	127'54
1'95038	0'42440	127'31	127'54
1'73248	0'37698	127'33	127'55
1'81923	0'39586	127'32	127'55
Mean		127'33	127'55
Mean of the three series ..		127'33	127'55

Tellurium from Bohemia.—Fifty grms. of tellurium from the Transylvania gold ores were precipitated by sulphur dioxide from hydrochloric acid solution, fused with potassium cyanide to remove sulphur, selenium, and any heavy metals; again precipitated from chloride solution by sulphur dioxide. It was then transformed into the basic nitrate, which was re-crystallised and ignited to oxide.

Tellurium from Copper Ores.—A quantity of tellurium residues from the electrolytic tanks of the Baltimore Copper Smelting and Rolling Co. was treated in alkaline solution with grape-sugar. The tellurium obtained was purified by precipitation from chloride solution by means of sulphur dioxide; this product was fused with potassium cyanide to separate it from sulphur, selenium, and the heavy metals, twice distilled in hydrogen, and after re-crystallisation as basic nitrate was converted to oxide.

Potassium Bromide.—The potassium used was prepared from Kahlbaum's pure material. It was repeatedly crystallised, and in each crystallisation the first portions and last portion were rejected.

Hydrobromic Acid.—The acid used was prepared from potassium bromide and sulphuric acid, the small amount of bromine formed being removed by means of phosphorus, and the resulting colourless acid repeatedly distilled.

Preparation of the Double Bromide of Tellurium and Potassium.—The tellurium oxide was dissolved in hydrobromic acid and the molecular proportion of potassium bromide added. The bright red anhydrous salt was crystallised from boiling solution, re-dissolved in pure water containing a small quantity of hydrobromic acid, and repeatedly crystallised from boiling solution.

In order to remove the last traces of moisture and hydrobromic acid, the salt was finely powdered and dried in vacuum desiccators over soda lime for a period of eight months. Tests made showed that the salt prepared in this manner is anhydrous.

Procedure.—The double bromide was weighed into a porcelain boat. The boat was covered with a loosely fitting piece of glass, and placed in a tube of Jena glass. A current of chlorine was passed through the tube, and heat was applied immediately below the boat. A low temperature was maintained for a short time, after which the temperature was gradually raised. After conducting a

brisk current of chlorine over the salt for an hour, the chlorine was replaced by hydrochloric acid gas, and the boat and the salt heated for an hour longer. Treatment of the material with hydrochloric acid gas is essential after the treatment with chlorine. Small amounts of tellurium oxide are produced in the potassium chloride by the action of the oxygen of the air remaining in the tube on the tellurium chloride first formed by the action of the chlorine on the original salt. It is impossible to volatilise this oxide from the resulting potassium chloride by heating in chlorine alone, but with hydrochloric acid gas $\text{TeO}_2 \cdot 2\text{HCl}$ is formed with the oxide, and is driven out of the boat. That any oxychloride is formed by heating tellurium tetrachloride in air or oxygen is highly improbable, and its doubtful existence will be shown in another place.

All weighings were made on a balance constructed by Troemner, having a capacity of 200 grms. and a sensibility with a minimum load of one fifty-fifth of a mgrm. All weighings are reduced to zero and vacuum. The slight change in weight of the porcelain boats used was constantly watched and corrections duly made. The following atomic weights were used:—1. Bromine, 79.96; chlorine, 35.45; potassium, 39.11. 2. The revised weights of the Atomic Weight Commission for 1909: Chlorine, 35.46; bromine, 79.92; potassium, 39.095.

It will be observed that the atomic weight of tellurium as given by use of 1909 figures for chlorine, bromine, and potassium appears as 127.55, which figure the author considers to be very close to the true ratio for tellurium.—*Journal of the American Chemical Society*, xxxi., No. 1.

THE POISONOUS GASEOUS EMANATIONS OF FERRO-SILICON.*

BEING A REPORT OF THE RESULT OF AN INQUIRY INTO THE CAUSE OF DEATH OF FIVE RUSSIAN IMMIGRANTS AT GRIMSBY.

THE importance of a consideration of this subject has been recently emphasised by the deaths of five Russian immigrants, who alone occupied the steerage of the s.s. *Ashton* during her voyage of some twenty-four hours from Antwerp to Grimsby, which latter place was reached on December 13. The ship carried a cargo of ferro-silicon, which was placed in the hold immediately underneath the fore between-deck hatchway accommodation occupied by the immigrants, which accommodation, by means of bulkheads, was shut off from the other part of the ship, except as regards the doors, which were under the control of the immigrants, and so in all probability were closed. The hatches above the accommodation were battened down and covered with tarpaulin, and the port-holes and ventilators were closed, so that if any gases emanated from the ferro-silicon below they would obtain easy access to the compartment occupied by the deceased above, and dilution could alone be effected by the possibility of the open doors.

The evidence given at the inquest by the steward was to the effect that the deceased appeared to be in good health on their arrival; that the usual supper was served to them, which was also partaken of by the crew; that two of the immigrants, who were girls, had tinned food in a pelisse which appeared to be pickled cherries, whilst one of the two men had half a loaf of bread and some polony. The fifth passenger was a boy aged eleven, the two men were respectively thirty-five and thirty-two years of age, and the women nineteen and fifteen. No complaint was made of illness on the part of the deceased, but on visiting them on the Sunday morning the steward found one of the girls to be vomiting, which he attributed to seasickness. On visiting her later he found that she was

dead, and upon calling the captain and with him making a further examination it was discovered that one of the men, the other girl, and the boy were also dead; the second man was alive, but he shortly after expired on deck, to which he had been removed. There was evidence that the deceased persons had vomited, and that some of them had cried for drink, otherwise no complaint was apparently made. The boy and the man were found dead on the floor, the two girls were discovered dead in their bunks, and the remaining man was found sitting in his bunk.

On the arrival of the ship at Grimsby she was boarded by the Port Medical Officer, Dr. W. Bulmer Simpson, who with commendable promptitude had the bodies removed to the mortuary, the ship disinfected, and retained in quarantine.

Dr. Simpson, who made the *post-mortem* examination, deposed that he found the lungs in all cases, with but one exception, congested with dark venous blood; that in that case one of the lungs was adherent to the chest-walls, whilst the other lung presented similar appearances to those found in the other cases. There were also some patches of ecchymoses on the lung surfaces; the intestines, both large and small, were empty, and that he had sent the stomachs of the several cases, with their contents properly secured, together with portions of the small intestines and two tins of apparently preserved cherries, to The Royal Institute of Public Health, London, for examination.

On Monday, December 14, 1908, these specimens were received at the Royal Institute, together with instructions that the examinations should be conducted with the view of determining the question as to whether cholera or ptomaine poisoning was the cause of death.

The five stomachs and corresponding parts of the small intestines were properly tied up and contained in five separate receptacles, marked Nos. 1, 2, 3, 4, and 5. The stomachs were found to be filled with a watery turbid liquid containing food-rests (cherries) and greyish-white flakes of mucus (especially in cases Nos. 1 and 5). The contents of the small intestines were less liquid than those found in the stomachs and had a greyish-yellow colour. The mucous membrane of the stomachs and of the small intestines showed a strong injection of the blood-vessels and was covered with mucus.

From a pathological point of view, therefore, the cases did not suggest evidence of cholera, as the "rice-water" like appearance of typical cholera contents was not presented.

Film preparations were made from the mucus flakes of the stomachs and intestines and these revealed amongst other bacteria, numerous vibrios (especially in Cases 1 and 5) in heaps, and even in "fish-in-stream" like arrangement, and thus the suspicion of cholera appeared to be justifiable.

The efforts for isolating the vibrios in question were for a long time without result, as they apparently, for some reason or other, were considerably weakened, and consequently could not be isolated from the original gelatin-agar and peptone water cultures, but they were subsequently isolated by means of sub-cultures from the second series of peptone water cultures, and even then only in Cases 1 and 2. These vibrios, which grew on gelatin and agar plates, in colonies indistinguishable from true cholera colonies, were subjected to a further examination. They gave the "cholera-red" reaction after twenty-four hours growth in peptone water, but tested with an agglutinating cholera-immune serum, they could not be agglutinated in a serum dilution of 1 in 100 within two hours, whilst in a control experiment the true cholera vibrios were agglutinated by the same cholera-immune serum in a dilution of 1 in 100 within a few minutes, and in a dilution of 1 in 500 in thirty minutes. Pfeiffer's reaction, also carried out with the vibrio under examination, a true cholera vibrio, and a true cholera-immune serum on four guinea-pigs, gave negative results, the vibrio not being dissolved. The vibrio, however, was found to be pathogenic for guinea-

* Communicated from the Laboratories of the Royal Institute of Public Health by the Principal, Professor WILLIAM R. SMITH, M.D., D.Sc., F.R.S. Ed. *Journal of the Royal Institute of Public Health*, January, 1909.

pigs; half a loop of the vibrio in 1 cc. broth intra-peritoneally injected into guinea-pigs killed them within eight to ten days; whilst one loop of the vibrio in 1 cc. broth intra-peritoneally injected, killed within three to four days. Thus it was proved that the vibrio isolated from the Grimsby cases, although closely resembling the cholera vibrio in its growth on media and giving the "cholera-red" reaction, and being pathogenic to guinea-pigs, was not the true cholera vibrio.

Since Ruffer's investigations, in El Tor, it is known that from the intestines of patients suffering from various diseases (diarrhoea, dysentery, pneumonia, rheumatism), but who had never had cholera nor been in contact with it, cholera-like vibrios may occasionally be isolated, and these five Grimsby cases furnish a confirmation of this statement. These cases are, therefore, of much interest, inasmuch as they prove the possibility of the existence of vibrios, closely resembling cholera vibrios, in the stomachs and intestines of presumably healthy persons.

In response to requests from the Institute, the following were received from Dr. Simpson:—

December 16: Portions of the lungs, specimens of the blood, and a small quantity of urine of the deceased.

December 17: A sausage, some syrup, small bottle of preserved fruit, and a small quantity (about 6 ozs.) of ferro-silicon.

December 19: A Winchester quart bottle of ferro-silicon.

Whilst the bacteriological examinations for the cholera vibrio were being made, the samples of food sent, together with the sausage and the contents of the stomachs and intestines, were subjected to examination for the detection of the presence of a food poison, or of food poison producing bacteria, belonging to the group of the *B. enteritidis* and *B. botulinus*, but both anaerobic and aerobic cultures (Drigalski, Conradi, Endo, Malachite green plates, &c.), and the experiments on animals (mice, rats, guinea-pigs) gave negative results. As the deaths had been of such a sudden nature, portions of the viscera, as well as the preserved fruit, sausage, &c., were chemically examined for alkaloids, arsenic, antimony, and the metallic poisons, but with negative results. Suspicion was now directed to a portion of the cargo as being a possible cause of death, owing to the poisonous gases which it was known to evolve. As the result of this, the portions of the lungs, blood, and urine were examined for arsenic, but without result. The blood was also spectroscopically examined for carbon monoxide, with like negative results.

With reference to the gases emanating from ferro-silicon the following experiments on animals were undertaken, viz.:—

1. A small quantity of the ferro-silicon received on December 17 was placed in the bottom of two glass jars, being moistened in the one case, but left dry in the other. Into each of these jars a mouse was then placed, resting on a piece of wire-gauze placed some distance above the substance. Both mice showed marked symptoms of dulness and somnolency, and the one before death disturbances of movement. The mouse over the moistened ferro-silicon died in four and a-half hours, whilst the one over the dry substance lived.

2. Four mice placed in a larger jar over moistened ferro-silicon also died within from six to ten hours.

3. Four guinea-pigs when placed over the moistened substance under similar conditions, died within ten hours.

4. A guinea-pig placed over a quantity of dry ferro-silicon also died, but this was possibly accounted for by the ferro-silicon becoming moistened with the animal's urine.

All these animals exhibited the symptoms previously mentioned, together with those of retching.

With reference to the *post-mortem* examination, the only common abnormal feature observed was congestion of the lungs, such as is usually seen in cases of death by suffocation. In a few cases pneumonia-like patches in the inferior lobes of the lungs were found. Two of the mice, however, showed enlargement of the spleen. The other organs of

all the animals exhibited no marked features. Microscopically, the lungs showed hyperæmia and albuminous exudation into the alveoli, whilst in the other organs no remarkable histological alterations could be noticed.

These animal experiments prove that ferro-silicon, when moist, readily evolves gases which are fatal to life. This substance is a coarse metallic powder, which, under ordinary circumstances, possesses no particular odour, but if confined, powdered, or moistened, a distinct phosphorous odour can be detected. It is manufactured by heating a mixture of iron-ore, quartz, coke, and lime in an electric furnace, and is used by steel-makers as a convenient method for the addition of silicon to certain grades of steel. A little consideration will give some indication of the nature of the poisonous gases likely to be formed when this product is moistened. Many minerals contain phosphoric acid and arsenic. Consequently, when such a mixture, as above described, is strongly heated, phosphides, arsenides, carbides, and silicides may be formed, and these may, under certain conditions, evolve phosphoretted hydrogen, arseniuretted hydrogen, acetylene, and silicon hydride.

In order to determine which of the above gases is mainly evolved when ferro-silicon is moistened, the following experiments were made:—

(a) Two hundred grms. of the powdered and moistened substance were placed in a horizontal glass tube, 19 in. long and 1 in. in diameter. This tube was connected with another tube about 11 in. long and a half inch in diameter, and filled with small pieces of potassium hydrate in order to absorb any sulphuretted hydrogen. Air was then gently drawn through the tube for about three hours and allowed to pass through a 10 per cent solution of silver nitrate contained in a De Koninck absorption apparatus. A dark precipitate was immediately produced in the silver solution and at the end of the period was considerable in amount. This precipitate might be due to all or any one of the above-mentioned hydrides.

(b) Experiment (a) was repeated, with the exception that the potassium hydrate tube was removed and ammoniacal cuprous chloride solution substituted for the silver nitrate. As no precipitate was formed in the copper solution it is evident that acetylene is not formed under these conditions.

(c) Experiment (a) was repeated, but in this case the gases were passed through nitric acid. The acid solution was evaporated almost to dryness, hydrochloric acid added, and the mixture evaporated to complete dryness. The addition of hydrochloric acid and subsequent evaporation to dryness was repeated and the residue dissolved in distilled water, when no trace of insoluble silica was found. Silicon hydride is, therefore, not evolved from moistened ferro-silicon at ordinary temperatures. Having excluded acetylene and silicon hydride from the gaseous mixture, there remains the possibility of phosphoretted and arseniuretted hydrogen.

(d) Some of the silver solution obtained in Experiment (a) was then filtered and the filtrate, which would contain arsenic (if present in the gases) as arsenic acid, was introduced into a Marsh-Berzelius apparatus, with the result that a slight mirror was obtained after prolonged heating. Some of the precipitate was then introduced into the apparatus, when the characteristic phosphorous flame was immediately produced, being most marked, and this, in spite of the facts that the heating of the glass tube was continued, which would tend to decompose phosphoretted hydrogen, and that the flame was burning at the end of a tube not furnished with a platinum jet. It is therefore evident that although arseniuretted hydrogen is produced in small quantities, the chief gas evolved is undoubtedly phosphoretted hydrogen, a gas which is stated to be so poisonous that 0.02 per cent of it in air is fatal to small animals within half an hour.

The result, therefore, of the enquiry into the cause of death of the five Russian immigrants on board the *s. Ashton* is that they died from the effects of gaseous emanations

tions from the cargo (ferro-silicon) mainly attributable to the presence of phosphoretted hydrogen.

This investigation is of great scientific interest, as possibly it is the first occasion in this country in which deaths have been known to be attributable to this cause.

As ferro-silicon is a substance the manufacture of which on a large scale has only been undertaken within the last few years, references in scientific literature to the poisonous nature of its gaseous emanations are very scanty.

The *Board of Trade Journal*, August 22, 1907, contains a reference to an enquiry made by Professor Cronquist, of Stockholm, into the cause of death of four persons on board the s.s. *Olaf Wijk*, which was carrying ferro-silicon as a part of its cargo, who gave as his opinion that death had been caused by the poisonous gases given off by this material, but he does not appear to have specified what gas or gases produced the fatal results.

On March 15, 1906, Bahr and Lehnkering (*Vierteljahrsschrift für gerichtliche und öffentliche Sanitätswesen*, xxxii., pp. 123-9), published the results of their examination of the bodies of two children, aged two and a-half and four and a-half, who had died on a Rhine steamer on a voyage between Mannheim and Duisberg. This vessel was carrying about 40 tons of ferro-silicon. These children had slept in a cabin situated just above the material, and it had been found necessary to light the stove. An ordinary wooden deck separated the children from the cargo, and it seems very probable that the stove had drawn the gases from the hold into the cabin. The symptoms before death were vomiting, thirst, and somnolency.

The *post-mortem* examination revealed no sufficient pathological, or anatomical, reason for death, the only abnormal appearance being congestion of the lungs. Chemically, no positive evidence of the presence of poisonous substances was obtained. This, of course, may be explained by the probability that phosphoretted hydrogen, which Lehnkering showed was given off in large quantities by the ferro-silicon of the cargo when moistened, is readily oxidised, and that phosphoric acid, the product of its oxidation, is a normal constituent of the human body. These authors also mention various deaths of persons on steamers carrying ferro-silicon, viz., one girl of fifteen years, one woman, one man, and a child of two years, which were most likely caused by phosphoretted hydrogen evolved by this substance, but owing to the absence of knowledge of the dangerous nature of the cargo, were not at the time so certified. Very little work appears to have been done respecting the physiological and pathological effect of phosphoretted hydrogen. The earliest reference appears to be in *Eulenberg Die Lehre von den giftigen Gasen*, 1865, p. 424, who says that 0.25 per cent of this gas in air is fatal to man.

In *Archiv. f. exp. Path. u. Pharm.*, xv., p. 438, is an abstract of a dissertation in Russia by "Brilliant," on the effects of this gas on various animals, and in vol. xxvii., p. 314, of the same journal appears a rather more detailed account of similar work performed by Schulz.

With reference to the toxicity, these authors state that 0.459 per cent PH_3 in air killed rabbits within about eighteen minutes. A striking but regular feature being that the animals soon became somnolent, and that ataxia and other disturbances of the movements were observed. Retching or vomiting was an almost invariable symptom, and the animals died finally in a state of stupor and asphyxia. The *post-mortem* of these animals showed no visible alteration of the elements of the blood, the cerebrum, and the spinal cord, but a degree of congestion of the intestinal organs and a high degree of hyperæmia in the lungs, partly accompanied with ecchymoses. Microscopically, the examination revealed congestion of the capillaries and albuminous exudation in the alveoli, but no noteworthy alterations in the other organs.

These *post-mortem* appearances furnish a confirmation of what was found in the animals experimented upon at the Royal Institute.

The pathological effects of such poisonous gases as

phosphoretted hydrogen and the like are at present so little understood that it has been determined to undertake further experiments in connection with this subject.

I cannot conclude this report without recording my great indebtedness to Dr. Hermann Dold, the Harben Demonstrator of Bacteriology and Comparative Pathology, and Dr. Charles E. Harris, the Demonstrator of Chemistry, upon whom the investigations mainly devolved.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 4th, 1909.

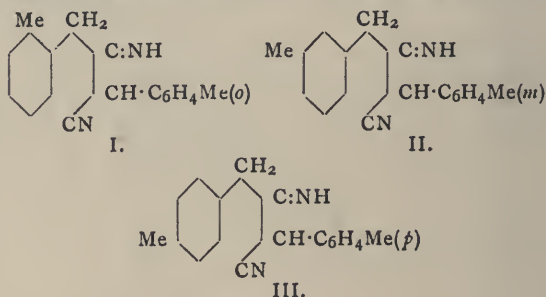
Sir WILLIAM RAMSAY, K.C.B., F.R.S., President,
in the Chair.

(Concluded from p. 92).

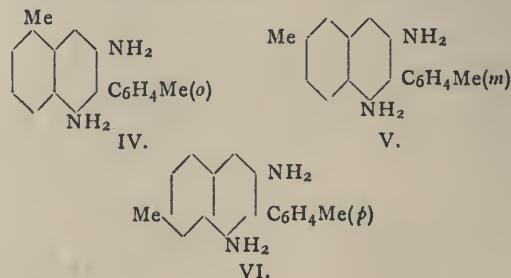
31. "The Formation and Reactions of Imino-compounds. Part VIII. The Formation of Methyl Derivatives of 2-Phenyl-1:3-naphthylenediamine from the three Tolyl-acetonitriles." By STANLEY ROBERT BEST and JOCELYN FIELD THORPE.

Previous experiments have indicated that the transformation of a benzenoid imino-nitrile into a derivative of 1:3-naphthylenediamine by the action of cold concentrated sulphuric acid is hindered if a methyl group is in the meta-position with respect to the carbon atom at which ring formation must take place. Experiments have now been made which furnish further instances of this hindering action.

The three tolylacetonitriles readily undergo intramolecular condensation, forming β -imino- α -cyano- α - γ -di-*o*-tolylpropane (I.), β -imino- α -cyano- α - γ -di-*m*-tolylpropane (II.), and β -imino- α -cyano- α - γ -di-*p*-tolylpropane (III.):—



and when these compounds are treated with cold concentrated sulphuric acid they are converted into the sulphates of 6-*o*-tolyl-1-methyl-5:7-naphthylenediamine (IV.), 6-*m*-tolyl-2-methyl-5:7-naphthylenediamine (V.), and 7-*p*-tolyl-2-methyl-6:8-naphthylenediamine (VI.) respectively:—



The yields of the naphthalene derivatives from the three iminonitriles are in accordance with previous observations. Thus the meta-derivative (II.), from which ring formation

is shown by the oxidation of the naphthalene derivative to 4 methylphthalic acid to take place in the para-position with respect to the methyl group, gives 80 per cent of the theoretical quantity of 6-*m*-tolyl-2-methyl-5:7-naphthylenediamine (V.), whereas from the ortho- and para-derivatives (I. and III.), from which ring formation has to take place in the meta-position with respect to the methyl group, scarcely more than 10 per cent of the naphthalene derivatives (IV. and VI.) are obtained under the same experimental conditions. The preparation and properties of the pyrimidine derivatives derived from the three tolyl-acetonitriles were described.

32. "The Effect of Contiguous Unsaturated Groups on Optical Activity. Part I." By THOMAS PERCY HILDITCH.

The chemical and physical behaviour of organic substances containing adjacent unsaturated groups has frequently been observed to be irregular, and, as is well known, the optical properties of refractive index and magnetic rotatory power exhibit anomalies in such cases. The present work is the first part of an investigation designed to find out if optical activity is subject to the same influences. From the collected observation of different workers, in the cases of terpene derivatives, optically active aromatic substances and optically active esters possessing conjugated unsaturated systems, the author showed that in many, but not in all, instances a pronounced increase in molecular rotatory power takes place. Further, from observations on the camphorates and camphor-3-sulphonates of a number of phenolic or amino-derivatives of substances containing a benzenoid residue adjacent to an ethylenic or carbonyl group, it is found that:—

1. Conjugation is accompanied by abnormal optical activity.

2. The effect reaches a maximum when the conjugated system is nearest to the asymmetric carbon atoms.

3. The effect is lessened as the proximity of the unsaturated groups to one another is lessened.

4. The effect is decreased, and sometimes completely destroyed, if a saturated group is interposed between the conjugated and asymmetric systems.

33. "The Miscibility of Solids." By ERNEST VAN-STONE.

While working on solid solutions with camphor, the author was led to develop the present theory. The explanation of the miscibility of solids is suggested by the Pope and Barlow theory, and may be stated as follows:—Two substances will show the greatest degree of miscibility, whose assemblages of spheres of atomic influence possess similar marshalling, and are capable of being partitioned into units possessing almost equal volumes, the volumes being the molecular domains.

This explanation applies to the miscibility of the elements and of compounds, both organic and inorganic.

The degree of miscibility of two elements depends on the closeness of agreement between the atomic volumes, and also on their valency values, and this accounts for the great tendency of the elements to form mixed crystals.

Where a difference in valency volumes exists, a slight expansion of the spheres composing the substance of lower valency volume causes the volume of the molecular unit to approximate closely to that of the substance of higher valency volume.

The freezing-point curves for camphor and borneol, benzoïn and benzil, and menthol and menthone have been obtained. The first pair of compounds forms solid solutions in all proportions, borneol raising the freezing-point of camphor continuously. Benzoïn and benzil show a curious behaviour, as the curve has two eutectic points with an intermediate horizontal portion. The curve for menthol and menthone appears to be continuous with a minimum point.

34. "Esterification Constants of Substituted Acrylic Acids." Part III. By JOHN JOSEPH SUDBOROUGH and JAMES MYLAM GITTINS.

The constants at 15°, using methyl alcohol with hydrogen

chloride as catalyst, have been determined for the following acids: *cyclo*-Hexanecarboxylic, phenylacetic, *n*- and *β*-phenylpropionic, *γ*-phenyl-*n*-butyric, *δ*-phenyl-*n*-valeric, furfurylpropionic, phenylbenzylacetic, undecylenic, oleic, elaidic, erucic, brassidic, phenyl-*β*-crotonic, allylacetic, sorbic, cinnamylideneacetic, hydrosorbic, cinnamylpropionic, *β*-phenylethylidenepropionic, phenylpropylideneacetic, *α*,*β*-oleic, *allo*-cinnamic, and tetrolic. The results confirm the conclusions previously drawn (*Trans.*, 1905, lxxxvii., 1840; 1907, xci., 1033).

The constants for *α*,*β*-unsaturated acids are remarkably low when compared with those for the corresponding saturated acids. *β*,*γ*-Unsaturated acids have constants somewhat larger than those for their saturated analogues, and double bonds which are still further removed from the carboxylic group have very little effect, so that there is practically no difference between the constants for the unsaturated and the corresponding saturated acid.

The effect of the reduction of benzoic to *cyclohexane*-carboxylic acid is remarkable, the constant being raised from 0.25 to 19.3.

A triple linking in the *αβ*-position has much the same effect as a double bond in the same position, and conjugate ethylene linkings have a somewhat greater retarding effect than an *αβ*-double linking.

35. "Brazilin, Hæmatoxylin, and their Derivatives. Part X. The Constitution of Trimethylbrazilone, of *a*- and *B*-Anhydrotrimethylbrazilone, and of the corresponding Derivatives of Hæmatoxylin." By WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

The authors described in detail the properties of the derivatives mentioned in the title with the object of proving that the constitutional formulæ assigned to them in the previous parts of this research are correct.

36. "The Preparation of Disulphides. Part III. The Nitrobenzyl Disulphides." (A Correction). By THOMAS SLATER PRICE and DOUGLAS FRANK TWISS.

In a recent communication on the nitrobenzyl disulphides (*Trans.*, 1908, xciii., 1401), the statement was made that "the three disulphides obtained in the course of this investigation have not been isolated before." This statement is erroneous so far as the ortho- and meta-disulphides are concerned, but it does not affect the subject-matter of the paper cited, since a new method of preparation of these disulphides is there given.

Jahoda (*Monatsh.*, 1890, x., 874) claimed to have prepared di-*o*-nitrobenzyl disulphide (this nomenclature is to be preferred to *o*-nitrobenzyl disulphide), but Gabriel and Stelzner (*Ber.*, 1896, xxix., 161) showed that Jahoda's product was really the mercaptan. They prepared the *o*-disulphide and found it to consist of yellow crystals which melted at 112—113°, these properties agreeing with those found by Gabriel and Posner (*Ber.*, 1895, xxviii., 1025) and Cassirer (*Ber.*, 1892, xxv., 3029). In 1901, Blanksma (*Rec. trav. chim.*, 1901, xx., 137) also prepared di-*o*-nitrobenzyl disulphide (this compound is not mentioned in *Abstr.*, 1901, lxxx., i., 461) and found that it melted at 110°. This melting-point agrees with that observed by the authors (109.5°), but they also find that on repeated crystallisation from alcohol the crystals become almost colourless, possessing only a slight yellow tinge.

Di-*m*-nitrobenzyl disulphide has been prepared by Lutter (*Ber.*, 1897, xxx., 1069) by oxidation of the corresponding mercaptan with iodine, and is described as consisting of yellowish white crystals melting at 103—104°. The melting-point agrees with that observed by the authors, but when pure the substance is almost colourless; individual crystals appear colourless, but in bulk they possess a faint yellow tinge.

Strakosch (*Ber.*, 1872, v., 692) claims to have obtained di-*p*-nitrobenzyl disulphide. The melting-point given, 89°, is quite different from that observed by the authors (126.5°), and does not correspond with the melting-points of the *o*- and *m*-compounds. The analytical results are also not satisfactory, 19.72 per cent of sulphur being found

instead of 19.05 per cent. Evidently the compound prepared by Strakosch was not the disulphide, and the authors are engaged in repeating his experiments. The pure substance possesses a colour similar to that of the *m*-disulphide.

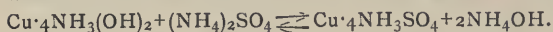
37. "*Derivatives of Naphthacenequinone.*" Part III. By DOROTHY HARROP, ROLAND VICTOR NORRIS, and CHARLES WEIZMANN.

In continuation of previous work (*Trans.*, 1907, xci., 1588), the authors have prepared a further series of naphthacenequinone derivatives.

38. "*The Nature of Ammoniacal Copper Solutions. Part II. The Solubility of Cupric Hydroxide in Ammoniacal Sulphate Solutions.*" By HARRY MEDFORTH DAWSON.

With the object of supplementing the information already obtained concerning the nature of ammoniacal solutions of copper salts (compare Dawson, *Trans.*, 1906, lxxxix., 1666; 1900, lxxvii., 1239), the author has measured the solubility of cupric hydroxide in ammoniacal solutions of ammonium and sodium sulphates, and of barium and sodium hydroxides.

Cupric hydroxide does not dissolve directly in pure ammonium sulphate solutions, and this is an indication that cupridiammonia compounds either do not exist or are not readily formed. In presence of ammonia the hydroxide dissolves readily, and ammonia therefore appears to be the primary cause of the solution process, cupritetraammonia hydroxide being thereby formed. This then reacts with the ammonium sulphate in the solution, the action consisting in the partial displacement of the ammonia from the sulphate by the stronger cupri-ammonia base, a condition of equilibrium being set up corresponding with the scheme:—



The solubility data are consistent with this view.

From a consideration of the quantities of ammonia which are necessary to dissolve cupric hydroxide in such quantity that the resulting solution contains copper and sulphate in equivalent proportions, the conclusion is drawn that optically clear solutions, prepared by adding ammonia (not in large excess) to copper sulphate solutions, are supersaturated with respect to cupric hydroxide. When such solutions are shaken with cupric hydroxide, a diminution in the copper concentration is actually observed. The deposited copper is supposed to be present in the original solution in the form of colloidal hydroxide.

The new observations are in agreement with the author's previous determinations of the chemical dissociation in ammoniacal solutions of copper salts on the basis of distribution measurements.

39. "*The Action of B-Rays on Photosensitive Solutions.*" By OTTO FLASCHNER.

The analogy between the action of light and that of β -rays on certain chemical reactions was pointed out and instanced in the case of two photosensitive solutions. The potential of an AgBr/KBr electrode rises under the influence of β -rays, and falls when the latter disappear. The higher the initial potential the more sensitive is the electrode towards light and β -rays.

The Eder's actinometric solution was the second type to be examined, and this is also influenced by β -rays.

40. "*The Rusting of Iron.*" By GERALD TATTERSALL MOODY.

In the experiments described by Tilden (*Trans.*, 1908, xciii., 1356), the author has lost sight of the well-known fact that commercial iron and steel invariably contain foreign substances, notably sulphur compounds, which on exposure to air and water at once furnish free acids. The rusting observed in Tilden's experiments, in which carbonic acid was excluded, was a result primarily of interaction between acids, formed by oxidation of sulphur compounds and other foreign constituents capable of furnishing acids on reaction with water and oxygen, and iron, the resulting

ferrous salt being subsequently oxidised with production of rust.

Tilden's experiments conclusively show that commercial iron after treatment with chromic acid no longer rusts in presence of water and oxygen, but the inactivity is wrongly attributed to the chromic acid rendering the iron "passive." The true explanation of the inhibitive effect of chromic acid is that it removes from the surface of the iron those constituents which would otherwise subsequently yield acids on exposure to water and oxygen. That Tilden's view that the iron is rendered passive is incorrect is conclusively shown by the readiness with which the iron rusts as soon as normal air containing carbonic acid or any other acid is admitted.

Tilden further states that after immersion for years of iron in dilute chromic acid, he has observed "no sign of rust or of dissolution of the iron either by change of colour or the formation of precipitate on adding excess of ammonia." In this connexion it must be pointed out that ferric hydroxide is readily dissolved by chromic acid, so that visible change could not be expected. Moreover, dilute solutions of iron in chromic acid do not afford a visible precipitate or a change of colour on addition of excess of ammonia. If, however, the solution is filtered after addition of ammonia, ferric hydroxide in appreciable quantity remains on the filter paper, and the dissolution of the iron is thereby made evident.

41. "*The Iodobenzenemonosulphonic Acids.*" Part I. By MARY BOYLE.

An account was given of the preparation and properties of 1:4:6-, 1:3:4-, 1:3:5-, and 1:2:4-di-iodobenzene-sulphonic acids; also of 1:2:3:5-, 1:2:4:5-, and 1:2:4:6-tri-iodobenzene-sulphonic acids. The acids were mostly prepared from the appropriate aminosulphonic acids by introducing iodine by means of iodine chloride and subsequently displacing the amino-group by iodine by the diazo-reaction.

It is noteworthy that all the iodo-diazo-sulphonates are coloured compounds, varying from very pale yellow in the case of the 1:4-acid to bright yellow in the case of the tri-iodo-acids.

The acids are all readily soluble in water, and several crystallise well, especially in presence of mineral acid. They furnish well-defined salts, which are only sparingly soluble in water. The sulphonyl chlorides crystallise well.

42. "*Contributions to the Chemistry of the Terpenes. Part IV. The Oxidation of Pinene with Mercuric Acetate.*" By GEORGE GERALD HENDERSON and JAMES WATSON AGNEW.

By the action of aqueous mercuric acetate at the ordinary temperature, pinene is converted into sobrerol, $\text{C}_{10}\text{H}_{16}(\text{OH})_2$, a compound formerly prepared by oxidising pinene with moist oxygen in sunlight, and sobrerol is oxidised to a hydroxyketone, $\text{C}_{10}\text{H}_{15}(\text{OH})\text{O}$, when heated with the same reagent. The hydroxyketone is reduced to sobrerol when dissolved in moist ether and treated with sodium, and it yields carvacrol on reduction with aqueous hydriodic acid in the cold. When heated for a short time with anhydrous oxalic acid, it yields carvone together with some carvacrol, and when it is oxidised with an acidified solution of potassium permanganate, terpenylic acid is obtained. Hence it is concluded that the hydroxyketone is 8-hydroxycarvotanacetone.

Sobrerol can also be prepared by the action of mercuric oxide on a cold solution of pinene in acetic acid, whilst if the solution is heated, the oxidation product is the hydroxyketone.

43. "*Formation of Heterocyclic Compounds. Part I. 1-Phenylpyrrolidine-2:5-dicarboxylic Acid from Adipic Acid.*" By HENRY RONDEL LE SUEUR.

The methyl or ethyl ester of 1-phenylpyrrolidine-2:5-dicarboxylic acid is readily obtained by the action of mono-ethylaniline on the corresponding methyl or ethyl ester of *aa'*-dibromoadipic acid.

1-Phenylpyrrolidine-2:5-dicarboxylic acid is crystalline,

and decomposes at 252° ; it is readily obtained by hydrolysis of its ethyl ester.

44. "The Influence of Solvents on the Rotation of Optically Active Compounds. Part XIV. Ethyl Tartrate in Benzaldehyde and in Quinoline." By THOMAS STEWART PATTERSON and DAVID PATERSON McDONALD.

The influence of benzaldehyde and of quinoline as solvents on the rotation of ethyl tartrate was described.

PHYSICAL SOCIETY.

Annual General Meeting, February 12th, 1909.

Dr. C. CHREE, F.R.S., President, in the Chair.

THE SECRETARY read the Reports of the Council and the Treasurer, which were adopted :—

Report of Council.

Since the last Annual General Meeting, ten Ordinary Science Meetings, two informal Meetings, and two Special General Meetings of the Society have been held. Of these, eleven were held at the Royal College of Science; one, that on March 27th, at the Northampton Institute, by invitation of Dr. R. M. Walmsley; one, that on October 23rd, at the National Physical Laboratory, by invitation of Dr. R. T. Glazebrook, F.R.S.; and one, that on November 13th, at University College, by invitation of Prof. F. T. Trouton, F.R.S. The average attendance at the meetings has been 61 as compared with 58 during the preceding year.

The Fourth Annual Exhibition of Apparatus by manufacturers was held on December 11th, when the attendance of Fellows and Visitors amounted to about 300. Greater advantage is now being taken of this event by exhibitors, and the attendance this year was much larger than hitherto.

Certain alterations to the Articles of Association have been introduced, more particularly in regard to the election of the Council. A copy of the revised Articles has been forwarded to every Fellow of the Society.

The number of Ordinary Fellows now on the roll, as distinct from Honorary Fellows, is 430, a decrease of 7 on the number last year; 12 new Fellows have been elected. There have been five resignations; the names of three Fellows have been struck off the list for non-payment of subscriptions; and the Society has to mourn the loss by death of two Honorary Fellows, namely, H. Becquerel and E. Mascart; also one of their Past-Presidents, Prof. W. E. Ayrton, one of their Secretaries, Prof. W. Cassie, and nine other Ordinary Fellows, namely, Lord Blythwood, Mr. S. Hall, Prof. A. S. Herschel, Mr. S. Joyce, Mr. F. J. M. Page, the Earl of Rosse, Capt. J. H. Thomson, Mr. J. F. Walker, and Dr. W. E. Wilson.

Report of the Treasurer for the Year 1908.

After the temporary boom of 1907 has succeeded another period of depression. It has been almost impossible, in spite of strenuous efforts, to collect any arrears of subscriptions, the amount under this head standing at £4 4s. as compared with £54 12s. in 1907. Only nine new Fellows have paid entrance fees as compared with 27 in 1907, and the amount from composition fees is unusually small. In other respects there is little change in the position or expenditure of the Society, except that last year's printing bill was unusually heavy, and the balance, allowing for liabilities, is slightly reduced in consequence. The provision of refreshments at the meetings has entailed a small additional outlay, but the catering has been carried out most economically, and the total expense for 1908 is little more than that for the exhibition of apparatus alone in 1907.

The following were elected as Honorary Fellows of the Society :—R. Benoit, Julius Thomsen.

The following Officers and Council were elected for the ensuing year :—

President—C. Chree, Sc.D., F.R.S.

Vice-Presidents—Those who have filled the Office of President together with W. Duddell, F.R.S.; Prof. A. Schuster, Ph.D., F.R.S.; S. Skinner, M.A.; W. Watson, D.Sc., F.R.S.

Secretaries—W. R. Cooper, M.A.; S. W. J. Smith, M.A., D.Sc.

Foreign Secretary—Prof. S. P. Thompson, D.Sc., F.R.S.

Treasurer—Prof. H. L. Callendar, M.A., F.R.S.

Librarian—W. Watson, D.Sc., F.R.S.

Other Members of Council—A. Campbell, B.A.; W. H. Eccles, D.Sc.; A. Griffiths, D.Sc.; J. A. Harker, D.Sc.; Prof. C. H. Lees, D.Sc., F.R.S.; T. Mather, F.R.S.; A. Russell, M.A., D.Sc.; Prof. E. Rutherford, D.Sc., F.R.S.; F. E. Smith; R. S. Whipple.

The PRESIDENT then delivered an Address.

He began by referring to the loss which the Society had sustained through the deaths of their ex-President Prof. Ayrton, and their Honorary Secretary Prof. Cassie. He referred to the assistance given to the Council by Mr. H. M. Elder, who discharged the duties of Secretary subsequent to Prof. Cassie's death until the appointment in the autumn of his successor, Mr. S. W. J. Smith. He spoke of the popularity of the Exhibition of Instruments, much of the success of which must be attributed to the Senior Secretary, Mr. W. R. Cooper and to the Physics Department of the Imperial College of Science and Technology. One of the incidents of the year had been the revision of the Articles of Association by the Council, whose alterations had been confirmed at statutory meetings. The President then proceeded to give an account of some work he had recently been engaged in, in connection with the reduction of the magnetic observations of the National Antarctic Expedition of 1902-4. This referred to an inter-comparison of simultaneous records of magnetic disturbances obtained in the Antarctic, and at the Observatories of Kew, Falmouth, Colaba (Bombay), Mauritius, and Christchurch (New Zealand). He exhibited a number of lantern-slides showing the sudden commencement of some magnetic storms, and the forms of some special types of disturbance observed in the Antarctic. Some results were given as to the directions and intensities of the disturbing forces to which the disturbances recorded at the different stations might be attributed.

NOTICES OF BOOKS.

The Elements of Physical Chemistry. By J. LIVINGSTON R. MORGAN, Ph.D. Fourth Edition. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1908.

THIS is one of the best elementary text-books on physical chemistry in circulation and should be put in the hands of every student of chemistry. Considerably shorter than the classical works on the subject, it covers the whole of the theory of the science in one volume, and while making no pretensions to being a work of reference it is sufficiently detailed for all the purposes of a first year student. The practical applications of physical chemistry are constantly pointed out, and the author's aim has been above all to make his readers so thoroughly conversant with the method of reasoning and the results obtained that they can readily use their knowledge as a tool in their own work. Many numerical results are discussed in the text and an abstract principle is hardly ever stated without being followed by actual experimental data from which the student is recommended to perform the calculations in question. Moreover, at the end of the book a collection of problems with answers is given to help more particularly the student who is working alone. The mathematics employed have been made as simple as possible, and even students who have had no higher mathematical training will find it comparatively easy reading.

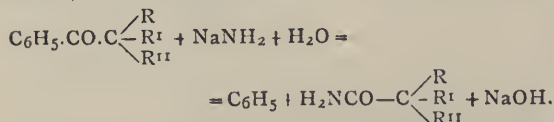
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences, Vol. cxlviii., No. 3, January 18, 1909.

General Method of Preparing Trialkylacetic Acids.—A. Haller and Ed. Bauer.—The trialkylacetophenones

of general formula $C_6H_5.CO.C \begin{smallmatrix} R \\ \diagup \\ R^I \\ \diagdown \\ R^{II} \end{smallmatrix}$, when heated with sodamide in a neutral solvent, such as benzene and its homologues, split up quantitatively, yielding the amides of trialkylacetic acids and an aromatic compound (hydrocarbon). The equation is—



The amides may readily be converted into acids by the action of sodium nitrite and sulphuric acid or of nitrosyl sulphate. The trialkylacetic acids thus formed are generally mobile liquids, with an odour only slightly resembling that of ordinary fatty acids. With the exception of pivalic acid, they are all nearly insoluble in water and can be distilled at the ordinary pressure without decomposition.

Rapid Preparation of Calcium Phosphide for the Production of Phosphoretted Hydrogen.—C. Matignon and R. Trannoy.—At a faint red heat, aluminium powder readily reduces tricalcic phosphate, the equation being $3(PO_4)_2Ca_3 + 8Al_2 = 3P_2Ca_3 + 8Al_2O_3$. The product is a brown mass, which, when left in the air, decomposes, giving phosphoretted hydrogen and a powder consisting of a mixture of alumina and the phosphide. By the action of water on calcium phosphide phosphoretted hydrogen is readily and rapidly obtained, the only impurity being traces of hydrogen.

Action of Sulphur Chloride on Metallic Oxides.—F. Bourion.—Sulphur chloride readily converts into chlorides even those metallic oxides with which a mixture of chlorine and sulphur dichloride gives poor results. The equation is $2MO + 2S_2Cl_2 = SO_2 + 2MCl_2 + 3S$, which shows that there is an excess of sulphur equal to three-quarters of that contained in the reacting sulphur chloride. Thus the lowest temperature at which the reaction occurs is determined by observing when a deposit of sulphur appears, and the reaction is commenced at this temperature; the temperature is afterwards gradually raised to a red heat. With MnO_2 , MnO , NiO , CoO , and the oxides of the rare earth the action begins before the boiling-point of sulphur is reached, and with chromium sesquioxide at a temperature above the boiling-point.

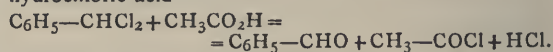
Colour Reactions of Dioxycetone.—G. Denigès.—In sulphuric acid dioxycetone condenses with mono or polyphenolic compounds and certain alkaloids, giving stable colorations. These reactions are very sensitive. With codein a blue colour is obtained, with resorcin at the ordinary temperature a tint resembling that of alkaline dichromates, with thymol blood-red, and with β -naphthol at the temperature of the water-bath a green coloration and a fluorescence of the same shade. The reactions with thymol and resorcin are particularly delicate.

Nature of Hofmann's Brominated Acetamide.—Maurice François.—The substance which Hofmann called brominated hydrated acetamide, and to which he attributed the formula $CH_3-CO-NHBr.H_2O$, really contains all its bromine in the form of hypobromite. It can be prepared by evaporating a mixture of hypobromous acid and acet-

amide, and when obtained thus preserves all its characteristic properties. It must therefore be regarded as acetamide hypobromite, and its formula must be written $CH_3-CO-NH_2.BrOH$. Moreover, the substance Hofmann prepared by removing water from the preceding compound at 50° , and which he called brominated acetamide, must be a hypobromous amide, $CH_3-CO-NHBr$; it is thus a secondary amide of acetic and hypobromic acids.

Products of Saponification of Dioxalsuccinic Ether. Isopyromucic Acid.—E. E. Blaise and H. Gault.—The authors prepared dioxalsuccinic ether by the action of two molecules of oxalic ether upon one molecule of succinic ether in presence of sodium ethylate, and saponified it with concentrated hydrochloric acid at the ordinary temperature. The product which is obtained by evaporating the aqueous solution has the formula $C_6H_4O_5$, and from this by the elimination of CO_2 isopyromucic acid is obtained. Apparently hydrochloric acid lactonises the ether as well as saponifying it, and the product of the action is a δ -lactone.

Preparation of Aldehydes and Anhydrides of Acids.—A. Béhal.—Acetic acid reacts with benzyl chloride giving benzyl acetate and hydrochloric acid. In presence of the chlorides of zinc, antimony, or copper one molecule of $C_6H_5-CHCl_2$ reacts with one molecule of acetic acid, giving benzoic aldehyde, acetyl chloride, and hydrochloric acid—



Large quantities of polymerisation products of benzoic aldehyde are also formed.

MEETINGS FOR THE WEEK.

- MONDAY, March 1st.—Royal Society of Arts, 8. (Cantor Lecture). "Modern Methods of Artificial Illumination," by Leon Gaster.
- Royal Institution, 5. General Monthly Meeting. Society of Chemical Industry, 8. "Some Requirements of a Colour Standard," by J. W. Lovibond, "Sulphur as a Cause of Corrosion in Steel," by G. N. Huntly.
- TUESDAY, 2nd.—Royal Institution, 3. "Evolution of the Brain as an Organ of Mind," by Prof. F. W. Mott, F.R.S.
- WEDNESDAY, 3rd.—Society of Public Analysts, 8. "Composition of Cider," by B. T. P. Barker and E. Russell. "Composition and Analysis of Chocolate," by N. P. Booth, C. H. Cribb, and P. A. E. Richards. "Determination of Petroleum in Turpentine," by J. H. Coste.
- THURSDAY, 4th.—Royal Institution, 3. "Problems of Geographical Distribution in Mexico," by Hans Gadow, F.R.S. Chemical, 8.30. "Action of Anhydrosulphuric Acid on Triphenylsilicic," by G. Martin and F. S. Kipping. "Ignition Temperatures of Gases," by H. B. Dixon and H. F. Coward. "Diazo-oxy-amido Compounds and the Influence of Substituting Groups on the Stability of their Molecules," by N. L. Gebbard and H. B. Thompson. "Tetraketopiperazine," by A. T. de Moulpiéd and A. Rule. "Alkaloids of *Senecio latifolius*," by H. E. Watt. "Miscibility of the Pyridene bases with Water and the Influence of a Critical Solution-point on the Shape of the Melting-point Curve," by O. Flaschner. "An Interpretation of the Hantzsch-Werner Hypothesis," by M. O. Forster and P. F. Dunn. "The Triazogroup—Part IX., Transformation of Cinnamoylazoimide into Cinnamylcarbamide (Cinnamylisocyanate), by M. O. Forster. "Preparation of Dichlorocarbamide," by F. D. Chattaway. "Interaction of Methyleneamines or Methyleneanilines and Carbimides or Thiocarbimides—Thiotetrahydroquinazolines Methylene Ureas, Dicarbimidomethylene Diamines and their Homologues," by A. Senier and F. G. Shephard.
- FRIDAY, 5th.—Royal Institution, 9. "Letters of Queen Victoria," by the Rt. Hon. Viscount Esher, G.C.B., &c. (By the gracious permission of His Majesty the King).
- SATURDAY, 6th.—Royal Institution, 3. "Properties of Matter," by Prof. Sir J. J. Thomson, F.R.S.

THE CHEMICAL NEWS.

VOL XCIX., No. 2571.

ON THE TETRAVALENCY OF OXYGEN.

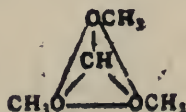
By H. STANLEY REDGROVE, B.Sc. (Lond.), F.C.S.

In the *Proceedings of the Chemical Society*, No. 350 (vol. xxv., p. 16) a "Note on the Constitution of the Carboxyl Group" appears by Miss Smedley, in which

"the constitution $\begin{array}{c} \text{O} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{OH} \end{array}$ is suggested for the carboxyl

group as better representing its physical and chemical behaviour." Some time ago, in connection with an examination of the thermal behaviour of organic oxygen compounds, a similar view of the carboxyl group suggested itself to the author of the present paper. It was noticed that an accumulation of oxygen atoms in a molecule is accompanied in certain cases by a lower molecular heat of combustion than would be expected from theory. For example, consider the successive substitution by the methoxyl group of the hydrogen atoms in methane; as will be seen from Table I., each successive methoxyl group produces a smaller increment in the molecular heat of combustion than the preceding. It was thought that the extra stability of these compounds containing two or more oxygen atoms might be explained by the hypothesis of tetravalent oxygen; for, if it be granted that oxygen can function as a tetravalent element (and for this there is a considerable amount of experimental evidence), there seems to be no good *à priori* reason against concluding that in compounds containing two or more oxygen atoms situated sufficiently near one another the secondary oxygen valencies are operative between such oxygen atoms, and consequently, that when such substances are burned, a certain amount of energy obtained otherwise as heat is employed in severing such oxygen links. According to this view methylal would be represented by the constitutional formula $\text{CH}_2 \begin{array}{c} \diagup \text{OCH}_3 \\ \text{O} \\ \diagdown \text{OCH}_3 \end{array}$, methyl

orthoformate by—



the carboxylic acids by the general formula suggested by Miss Smedley, the esters of such acids by the general formula $\text{R.C} \begin{array}{c} \diagup \text{O} \\ \text{O} \\ \diagdown \text{O.R} \end{array}$, &c.

However, in attempting to consistently carry out this hypothesis, difficulties were raised equal to those which were obviated by it; and after careful consideration it was concluded that the hypothesis could not be justified by the thermal data under consideration. In view, however, of Miss Smedley's Note it will not be without interest to give a brief account of those considerations which suggested the above hypothesis and the difficulties which it raised; in the hope that some explanation of the anomalies herein noticed may be forthcoming.

Arguments for the Hypothesis.

1. In the examination of the thermal behaviour of ketonic oxygen three values were obtained for the constant

TABLE I.

Substance.	Formula.	M.H.C. (a) Cals.	Difference. Cals.
Methane	CH_4	210.8	
Dimethyl ether .. .	$\text{CH}_3.\text{OCH}_3$	348.2	137.4
Methylal	$\text{CH}_2(\text{OCH}_3)_2$	474.9	126.7
Methyl orthoformate.	$\text{CH}(\text{OCH}_3)_3$	598.0	123.1

TABLE II.

Carbon dioxide.. ..	CO_2	0.0	
Carbonyl chloride ..	COCl_2	42.1	42.1
Carbon tetrachloride .	CCl_4	76.5	34.4

TABLE III.

Carbon dioxide.. ..	CO_2	0.0	
Carbonyl sulphide ..	COS	130.7	130.7
Carbon disulphide ..	CS_2	264.5	133.8

(a) All the experimental molecular heats of combustion given in this paper are due to Thomsen, and have been corrected for constant volume. It should be borne in mind that, since this data relates to gaseous compounds, the arguments which follow will hold, strictly speaking, only in the case of gaseous substances. In the liquid state many organic oxygen compounds appear to be associated, and this association may probably be due to tetravalent oxygen; if this be so, then, since the secondary oxygen links are employed in binding together smaller molecules into more complex ones, it is obvious that they cannot at the same time (or at least, that both secondary links cannot) be operative within the smaller molecules of such substances.

ω_2^* —for aldehydes $\omega_2 = 87.7$ cal., for ketones $\omega_2 = 91.4$ cal., for carbon dioxide, mono-basic carboxylic acids and their esters $\omega_2 = 105.4$ cal. This apparently anomalous behaviour was explained in terms of the theory of dynamic isomerism; and there can be little, if any, doubt that the presence of the enolic form is one factor producing an abnormally high molecular heat of combustion in the cases of aldehydes and ketones. However, it might well be supposed, since the value $\omega_2 = 105.4$ cal. has been obtained only in the cases of compounds containing two oxygen atoms, that the highness of this value (and hence the lowness of the molecular heats of combustion calculated thereby) may be due in part to the presence of tetravalent oxygen in such compounds. This suggestion is strengthened by the following consideration.

2. Carbonyl chloride is represented by the formula COCl_2 , i.e., $\alpha - 2\chi - \omega_2$, its molecular heat of combustion is 42.1 cal., which gives still another value for ω_2 , namely, 97.7 cal. Now, carbonyl chloride cannot be subject to dynamic isomerism and, since the affinity of oxygen for chlorine is small, we should not suppose that there is operative any secondary link between the oxygen and chlorine atoms contained in its molecule. Hence, it might be concluded that this value (97.7 cal.) is the true value of ω_2 ; the difference between it and the higher value being the thermal equivalent of an $\text{O}:\text{O}$ link; and the divergence in the cases of aldehydes and ketones being due to the presence of the enolic form which theoretically would have a relatively high molecular heat of combustion.

This argument can be otherwise presented by a comparison of the thermal behaviour of carbon dioxide, carbonyl chloride, and carbon tetrachloride (see Table II.). It will be seen that the substitution by oxygen of the first two chlorine atoms in carbon tetrachloride produces a less decrease in the molecular heat of combustion than

* For the meaning of this and other constants mentioned in this paper, and for an explanation of the author's method of calculating thermochemical constants, reference may be made to back numbers of the *CHEMICAL NEWS*, but a full and complete account will be found in the author's monograph "On the Calculation of Thermo-Chemical Constants" (Arnold).

TABLE IV.

Substance.	Formulae.	M.H.C. found. Cals.	M.H.C. calculated. Cals.	Difference. Cals.
Methylorthoformate	$\text{CH}(\text{OCH}_3)_3$ $4\alpha - 3\omega$	598.0	617.0	+19.0
Dimethyl carbonate	$\text{O}:\text{C}(\text{OCH}_3)_2$ $3\alpha - 2\omega - \omega_2$	357.0	$\begin{cases} 376.2 (\omega_2 = 105.4 \text{ cal.}) \\ 383.9 (\omega_2 = 97.7 \text{ cal.}) \end{cases}$	$\begin{cases} +19.2 \\ +26.9 \end{cases}$
Diethyl carbonate..	$\text{O}:\text{C}(\text{OC}_2\text{H}_5)_2$ $5\alpha - 2\beta - 2\omega - \omega_2$	672.9	$\begin{cases} 692.8 (\omega_2 = 105.4 \text{ cal.}) \\ 700.5 (\omega_2 = 97.7 \text{ cal.}) \end{cases}$	$\begin{cases} +19.9 \\ +27.6 \end{cases}$
Acetic anhydride ..	$(\text{CH}_3\text{CO})_2\text{O}$ $4\alpha - 2\beta - \omega - 2\omega_2$	459.5	$\begin{cases} 452.0 (\omega_2 = 105.4 \text{ cal.}) \\ 467.4 (\omega_2 = 97.7 \text{ cal.}) \end{cases}$	$\begin{cases} -7.5 \\ +7.9 \end{cases}$

the similar substitution of the last two, which appears to be explicable if we assume the existence of an O:O link in the carbon dioxide molecule. (We take for granted that no secondary chlorine links are operative in the carbon tetrachloride molecule). An examination of the corresponding compounds containing sulphur in place of chlorine shows a regular behaviour (see Table III.). But if we regard oxygen as exerting a tetravalent function in carbon dioxide, then, *a priori*, we should regard sulphur as tetravalent in carbonyl sulphide and carbon disulphide; and since the thermal effect of these secondary links is in any case small, the differences between an O:O and an O:S link, and between an O:S and an S:S link respectively would be practically equal, and would not cause the molecular heat of combustion of carbonyl sulphide to diverge more greatly from the mean between the molecular heats of combustion of carbon dioxide and carbon disulphide than it actually does.

3. The molecular heats of combustion of methyl orthoformate and dimethyl and diethyl carbonate are considerably lower than expected by theory (see Table IV.).

Using the constants $\omega = 75.4$ cal., $\omega_2 = 105.4$ cal., these three substances give an almost constant divergence, which might be explained by assigning them formulæ containing tetravalent oxygen; but acetic anhydride—another substance containing three oxygen atoms—has a molecular heat of combustion greater than the theoretical! However, if we apply the hypothesis under consideration consistently, we must use the constant $\omega_2 = 97.7$ cal. (see above), for, if this hypothesis be true, in using the higher value an O:O link has been allowed for. If this constant is employed the theoretical molecular heat of combustion of acetic anhydride does exceed by a small amount the experimental value, but the four substances in question give by no means consistent divergences.

Arguments against the Hypothesis.

1. On attempting to work out the hypothesis quantitatively consistent results cannot be obtained. This inconsistency is particularly marked in the case of the values obtained for the influence of the secondary links of three oxygen atoms. The carbonic esters give the values 26.9 and 27.6 cal., methyl orthoformate 19.0 cal., and acetic anhydride only 7.9 cal.

2. It must be noticed that many of the apparent anomalies upon which the hypothesis depends can be otherwise explained. The behaviour of the aldehydes and ketones appears to find a satisfactory interpretation in the theory of dynamic isomerism alone; the divergence in the case of methylal is small, and the value of ω calculated from its molecular heat of combustion differs from the mean less than does that obtained from the molecular heat of combustion of diethyl ether; and the divergence in the case of acetic anhydride is small, and this substance is still exceptional even if the hypothesis in question be adopted.

3. The most fatal objection to the hypothesis herein outlined, however, is as follows:—It has been tacitly assumed in all the arguments above that when oxygen becomes tetravalent the thermal value of the two primary valencies remains unaltered, but *a priori* it seems far more likely that the total valency-energy of the oxygen atom will remain unaltered, and hence, that when oxygen functions as a tetravalent atom, the thermal value of its

two primary valencies will be decreased, and if this be so all the above arguments for the hypothesis entirely break down. At any rate we must not assume that the value of the two primary oxygen valencies when oxygen is tetravalent is equal to the value of the two valencies of divalent oxygen until proof be forthcoming; and this objection will hold good in the case of all physico-chemical properties and not merely molecular heats of combustion and formation.

The Polytechnic, Regent Street, W.

CHEMICALLY TREATED FLOURS.*

By E. F. LADD, Food Commissioner and Chemist.

DURING the past few years there has been a great deal of discussion with regard to the bleaching and chemically ageing of flours. On the one hand it has been claimed that the process of artificial bleaching brings about results similar to those of natural ageing of flour; while, on the other hand, it has been contended that there is introduced into the flour a powerful chemical agent which brings about untoward changes in the flour itself, rendering it less nutritious, and that the flour so artificially treated contains an active chemical constituent which acts as a preservative. Believing that the information which has been secured, as the result of experimental work carried on for the past two years, is of such a nature that it should be given to the public, the writer has concluded to present the data in substantially the same form and manner as presented before the District Court at Fargo, North Dakota, in answer to the injunctive proceedings, and also as presented before the Honourable Secretary of Agriculture and the Board of Food and Drug Inspection at Washington on November 18 to 23, 1908. The information is therefore presented in two parts, I., The Bleaching of Flour; and II., The Effect of Bleached Flour Extracts on Rabbits.

I. BLEACHING OF FLOUR.

By E. F. LADD and H. P. BASSETT.

The bleaching of flour or the effect of nitrous acid upon the different constituents of a flour is a subject which has been but little investigated, and is a field which promises to yield interesting results where the investigations are pushed along new lines.

During the past few years the millers of North Dakota, as well as of the entire country, have been using nitrous acid fumes or nitrogen peroxide produced in different ways for bleaching or "ageing of flours." It seems that no other bleaching agent lends itself so readily to the use for this particular purpose.

Nearly all the work done along this line has been undertaken to determine the effect on the gluten expansion, volume of loaf, blending of bleached flour with higher grades of flour, &c. With the exception of a paper submitted by Prof. J. H. Shepard, Chemist of the South Dakota Experiment Station and Food Commission, nothing has been done to determine the effect of this highly poisonous gas, nitrogen peroxide, or of the resulting pro-

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ducts on digestion. This, therefore, may be considered the most vital point to be considered, because it is here that the deleterious effects, if such there are, will be produced upon man. On certain phases of this question considerable work has been done by Ladd and Stallings and by Prof. Alway, whose results are published as Bulletin No. 102 of the Nebraska Experiment Station. Prof. Alway, however, does not seem to have investigated the effects upon the nitrogenous constituents or to have used samples of flour bleached to the extent found upon the market in this state, and he therefore concludes that the use of nitrous acid is harmless since only very small quantities of the reagent is used in the bleaching of flours.

Experiments with Bleached Flour.—Our early experiments were to determine the amount of nitrous acid or nitrites present in samples of bleached flour, and after a number of preliminary experiments with methods and samples of flour, a sample of the commercially bleached flour for trade from the Valley City Mill was found to contain:—

In 5 grms. 0.0034 mgrm. nitrogen.
Calculated as sodium nitrite. . . 0.01671 mgrm.

In flour for one loaf of bread
(373 grms.) 1.24656 mgrms. NaNO_2 .

This would be 6.8 parts of nitrogen as nitrite nitrogen per million.

In a sample of the clear, from the same mill, as bleached for trade, there was found:—

In flour for one loaf of bread
(373 grms.) 2.4159 mgrms. NaNO_2 .

This would be 13.14 parts of nitrogen as nitrite nitrogen per million or 65.7 parts as sodium nitrite.

In a sample of flour taken from a Minnesota Mill there was found in the amount for one loaf, 373 grms., 1.313146 milligrms. as NaNO_2 .

Amount in Bread.

A sample of bread, produced from the flour as commercially bleached from the Valley City Mill, was analysed to determine the amount of nitrites present, when calculated as sodium nitrite. 373 grms. produced a loaf weighing, approximately, 18 ounces or 509 grms., and was found to contain 0.44352 milligram as NaNO_2 , or, approximately, one-third of the amount originally found in the flour.

A sample of bread produced in the same way from over-bleached flour, from the Valley City Mill, showed 3.546 milligrms. NaNO_2 , or, slightly less than one-third of that found in the flour.

Effect of Bleaching on Fat.

Fat extracted from the unbleached Valley City Mill flour that has stood in the laboratory for nine months gave iodine No. (Hanus Mod.) 101.2°. A sample of the same flour, bleached, and which had stood in the laboratory for nine months after bleaching, gave iodine No. (Hanus Mod.) 84.1°. Other tests showed similar results. The oil from the bleached sample was more stringy and like the results of the action of the nitrous acid or nitric acid, or the combined action of the same in producing elaiden.

Nitrogen combined with Oil.

Two samples of flour, the one bleached and the other unbleached of the same, were extracted with ether. About 200 grms. of flour were used, the ether distilled off, leaving the fat, and the residue taken up in re-distilled petroleum ether solution, carefully filtered, and the petroleum ether thoroughly evaporated off, thus getting rid of any impurities which may have been originally in the oil from ether extraction.

The tests for the presence of combined nitrogen and fat were made as follows:—

A piece of well cleaned metallic sodium was strongly heated in an ignition tube, and three drops of the wheat

flour oil was then allowed to fall upon the partly vaporised sodium. When cool, the contents of the tube were first treated with a little alcohol and then with water. This solution was then filtered, treated with a few drops of sodium hydroxide solution and with ferrous sulphate solution, then boiled for a minute or two. Just enough of dilute hydrochloric acid was added to dissolve the precipitate, and, finally, a drop or two of ferric chloride solution was added; the presence of nitrogen being indicated by a precipitate of Prussian blue.

Oil from unbleached flour No nitrogen.

Oil from bleached flour Considerable combined nitrogen.

Numerous other tests made upon the oil from bleached and unbleached flour gave similar results.

Tests were next made upon the oil extracted from bread produced from bleached and unbleached flour without the addition of any foreign fat. The loaf was dried, ground to fine meal, extracted with ether, and purified with petroleum ether, as previously described, with results as follows:—

Oil from bread, unbleached. No combined nitrogen.

Oil from bread, bleached. Combined nitrogen.

The amount of nitrogen in the oil from the sample of bread made from the bleached flour was less than in that of the flour from which the bread was produced.

Nitrous and Nitric Acid Present.

Tests were made showing the presence of both nitrous and nitric acid, or nitrites and nitrates, as reacting material in flour, which had been bleached by the use of nitrogen dioxide or tetroxide. In numerous of the experiments made, from one-third to one-half of the amount of nitrites found in the flour are recovered in the bread made by the usual process with yeast as a leavening agent. In the case of biscuit, rolls, and like products where baking powder or soda is used and in the thinner products, the nitrites are in a large measure destroyed or by oxidation changed to nitrates.

The Effect of Bleaching on Digestion.—In Prof. Shepard's work he investigates the effect of nitrous acid on the action of the digestive enzymes on pure corn starch. This, however, leaves out the action on flour, bread, and other products where protein bodies, and in some cases starch, are present, and on this point the following work is reported.

Effect of Bleaching on Digestion of Gluten and Bread.

The pepsin solution used in these experiments was prepared according to the directions given in Simon's "Physiological Chemistry," page 450, which is as follows:—

The following three solutions were prepared:—

A.—To 294 cc. of water 6 cc. of hydrochloric acid (1.20 sp. gr. diluted to 10) was added.

B. To 100 cc. of solution A, 0.06 gm. of pepsin was dissolved.

C. 90 cc. of solution A was brought to 40° C. in a digestion oven and 10 cc. of solution B was then added.

These experiments were carried out in the following manner:—

A test-tube $\frac{3}{4}$ inch in diameter was cut off, forming a short tube about 3½ inches long; in the bottom of this a hole was blown to allow the digestion solution to come in contact with the substance to be digested. In the bottom of this tube was placed a plug of glass-wool, packed with a glass rod, and on this plug was placed the gluten or bread to be digested. This was then immersed in the flask containing the digestion solution, and the time noted until the bread or gluten had disappeared. The time could not be accurately determined, but when there was a marked difference, as is shown in some cases, a relative figure can be determined.

Eight trials were made in the manner described, using the raw gluten obtained by washing out 10 grms. of com-

mercially bleached flour by the usual method and treating with 200 cc. of solution C. The following results were obtained :—

Gluten from Bleached Flour.

No. of Tube.	Time of Digestion.
1.	8 hours.
2.	8½ hours.
3.	9 hours.
4.	Left over night and the oven cooled down.
5.	Started 7.30 a.m., and allowed to run until 6.0 p.m., and hardly could be said to be fully digested.
6.	9 hours.
7.	10 hours.
8.	8 hours.

Ten trials were made under the same conditions as in the case above, using the gluten from 10 grms. of unbleached flour with the following results :—

Gluten from Unbleached Flour.

No. of tube.	Time of digestion.	
	Hrs.	Mins.
1.	4	0
2.	4	30
3.	4	0
4.	4	0
5.	5	0
6.	4	30
7.	5	30
8.	6	0
9.	6	0
10.	6	0

In the above cases raw gluten was used, and raw material of this character is much harder to digest than when cooked in some form, so it was thought advisable to try the action of the digestion fluids on baked gluten.

The baked gluten from 10 grms. of flour was treated in the manner previously described, but no such marked difference could be detected as the digestion was much more rapid and the difference in time could not be noted as well.

Baked gluten from bleached flour was first tried with the following results :—

No. of tube.	Time of digestion.	
	Hrs.	Mins.
1.	3	0
2.	3	30
3.	2	30
4.	2	30
5.	3	30
6.	3	30

It will be noted that two of the above trials required only two and a-half hours, but in most cases over three hours were required.

Baked gluten from unbleached flour was next tried in the same manner with the following results :—

No. of tube.	Time of digestion.	
	Hrs.	Mins.
1.	2	0
2.	1	45
3.	2	0
4.	2	30
5.	2	0

In only one case did the baked gluten from unbleached flour require over two hours.

The next trials along this line were carried out on bread made from each of the flours. The following table will give the results obtained with bread made from bleached flour :—

No. of tube.	Time of digestion.	
	Hrs.	Mins.
1.	2	0
2.	1	45
3.	2	0

The results with the bread made from the unbleached flour are given below :—

No. of tube.	Time of digestion.	
	Hrs.	Min.
1.	2	0
2.	1	30
3.	1	45

It will be noted that the time of digestion was in favour of the unbleached flour, but the times of digestion are so close that the results are not necessarily as definite as in the case of raw gluten.

(To be continued).

AN APPARATUS FOR DECANTING AND FILTERING.

By J. HUDIG.

WHEN decanting or filtering by hand considerable difficulties are often encountered, whilst by the constant moving of the vessel holding the liquid and the precipitate, the latter is stirred up so that small quantities of the precipitate pass over into the filter, and thus partially clog the same. If easily movable or colloidal precipitates are to be dealt with, it will occasion a considerable delay in the filtration.

As keeping the filter constantly filled is an absolute necessity for rapid filtration, it is difficult to effect several filtrations simultaneously, especially when the liquid to be filtered is at a high temperature.

I, however, succeeded in constructing an apparatus by which several filtrations can be effected simultaneously. The apparatus I have used for two years is shown by Fig. 1.

On a shaft, which is rigidly fixed to a stand, several holders are rotatively arranged by means of sockets. The holders consist of a wooden block. The flask upon the block is held by an adjustable spring, which is prolonged upwardly and provided with a pivoted perforated tension plate. The wooden block is provided with a clamping spring for the purpose of attaching a glass rod for forming drops and guiding the liquid. The neck of the flask is held close to the glass rod.

At the side of the socket a wooden wheel is fitted, which engages with a screw spindle movably arranged in a guide; this guiding piece is rigidly fitted to the shaft. The free ends of the screw spindle are displaceable longitudinally in the guiding piece, and for the purpose of maintaining the same in any desired position a clamping nut is provided. The screw spindle is thus free to turn, whilst a longitudinal displacement of the same is prevented by the fixing of the stop screw. The manipulation is as follows :—The flask with the fluid is put on the block, and then the clamping ring is closed by means of the plate, thus firmly holding the flask, which has an inclined position. After some time the precipitate settles to the bottom of the flask. Now the clamping nut is unscrewed so that the screw spindle can be pushed down, which puts the wheel in rotation, and so the flask is raised until the liquid nearly flows out of the mouth, after which the clamping nut is fastened again. Now, a glass rod is held to the neck of the flask by means of the spring. Then the spindle is slowly rotated by means of its button in order to pour out the liquid which is to be filtered. The supply of the liquid can be exactly regulated so that the liquid flows for some time, and the filter remains constantly filled. Nothing of the precipitate is stirred up.

Finally, the flask can be lifted so high that all the liquid has been poured out and the precipitate has been completely freed from liquid. For the purpose of washing, the flask is turned back and the washing fluid sprayed in. Now, in order to shake the flask, the clamping nut is released, and the spindle is moved to and fro. Then the filtering is con

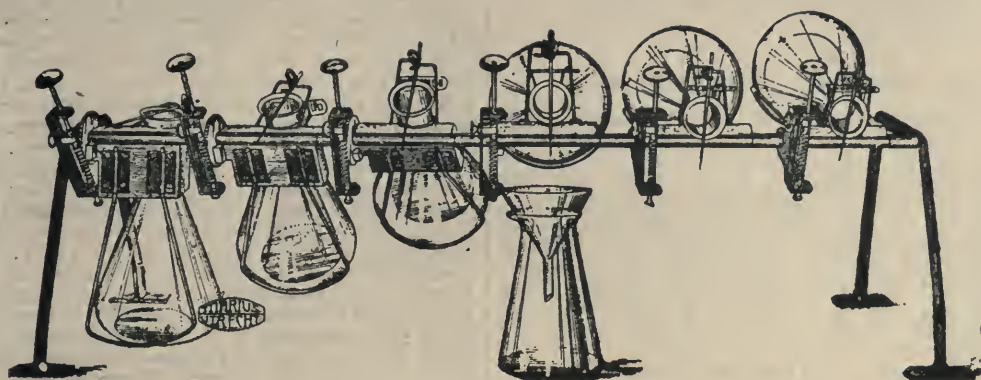


FIG. 3.

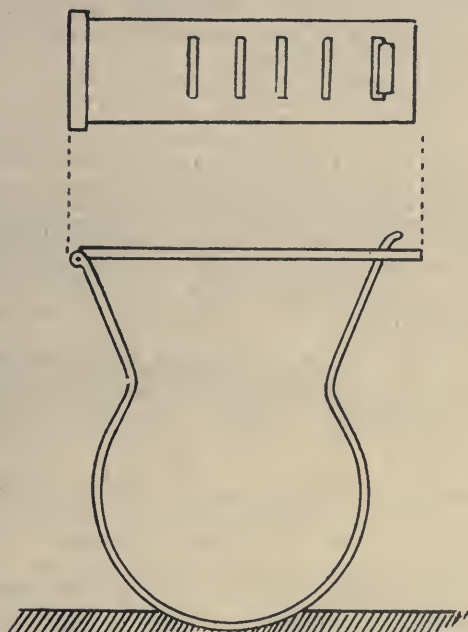


FIG. 2.

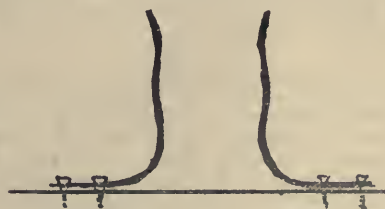


FIG. 3.

tinued as described above, and finally the precipitate can be sprayed together with the washing liquid into the filter.

It is easy to perceive that with this apparatus the following advantages can be obtained:—

1. The fluid is decanted absolutely free from precipitate.
2. The filter is constantly filled.
3. The precipitate can be completely freed from liquid.
4. Several filtrations can be simultaneously effected.
5. Working in this way the manipulation of decanting is much more convenient and also less tedious than ordinary filtering by hand.

Some of my experiments may be illustrated.

Determining P_2O_5 in Thomas Slag.—For instance, when the acid solution of ammonium molybdate is added, and the mixture boiled in order to precipitate the $(NH_4)_3PO_4 \cdot 12MoO_3$ well, I put six flasks upon the blocks, and fasten them (each flask contains ± 160 cc.), filter, wash, and bring the precipitate upon the filter within twenty minutes.

Then the flasks are loosened, the solution of the yellow precipitates in NH_3 filtered into them, neutralised, and the phosphoric acid is precipitated by magnesia mixture. The flasks are again put into the apparatus and treated as before. All can be done in a quarter of an hour.

Specially I have had experience with colloids, as $Fe(OH)_3$, $Al(OH)_3$, MnO_2 , $Mn(OH)_2$, and several sulphides. Formerly I took for one filtration of MnO (which may not come into contact with the air) in 400 cc. liquid about two hours; now I easily effect three of them simultaneously in about half-an-hour.

When operating with beakers springs of the same shape as shown in Fig. 1 can be used, only they must be somewhat bigger. Fig. 2 shows these springs in detail. One spring can be used for several sizes of beakers.

I now use when operating with Erlenmeyer flasks a spring as is shown by Fig. 3. A caoutchouc ring must be put round the neck of the flask and then placed upon the block, so that the ring is put just before or within the spring.

At the experiment station of Groningen, where often several analyses are to be done simultaneously, two apparatus for six filtrations have been of great advantage.

Different apparatus for six, four, and two filtrations are now constructed by Mr. Marius, of Utrecht (Holland). Shortly this apparatus, which has been licensed in England, will be also manufactured by an English firm.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 1st instant, Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, in the Chair. The Right Hon. Sir George Wyatt Truscott, Lord Mayor, Mr. A. E. Garrett, Mr. D. Jones, Mr. E. Lunge, Dr. J. H. Openshaw, and Miss Power were elected Members. The special thanks of the Members were returned to Mrs. Wigan for her donation of ten guineas to the Fund for the Promotion of Experimental Research at Low Temperatures. The Honorary Secretary reported the death of Prof. Julius Thomsen, the distinguished Danish chemist, and an Honorary Member of the Institution, and a resolution of condolence with the family was passed.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 18th, 1909.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

THE PRESIDENT referred to the loss sustained by the Society in consequence of the death of three Honorary and Foreign Members, Professor Wolcott Gibbs (elected May 3rd, 1866; deceased, December 9th, 1908), Professor Emil Erlenmeyer (elected February 1st, 1883; deceased, January 22nd, 1909), and Professor Julius Thomsen, F.R.S. (elected May 18th, 1876; deceased February 13th, 1909). The death of Professor W. H. Huddleston, F.R.S., was also announced.

The President stated that the Council had recommended Professor Dr. Georg Lunge as an Honorary and Foreign Member, and that his election would be balloted for at the next Ordinary Scientific Meeting of the Society. Fellows wishing to participate in the forthcoming Celebration of Professor Lunge's seventieth birthday on September 15th, 1909, should forward their subscriptions to Professor E. Bosshard, Eidgenössisches Chemiegebäude, Zürich.

Messrs. D. Avery, W. C. Birch, H. Green, and H. Main were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Hugh Garner Bennett, M.Sc., 13, Spring Grove Terrace, Leeds; Frank Playfair Burt, B.Sc., Elmhyrst, Weston-super-Mare; Reginald Cyril Herbert Cooke, 17, St. Edmund's Terrace, Regent's Park, N.W.; Henry Jermain Maude Creighton, M.A., Halifax, Nova Scotia, Canada; Philip Henry Crewe, Glencairn, Woods Moor, Stockport; John Frederick Haws, Parkfield Villa, Newton-by-Frankby, Cheshire; Reginald Vernon Hickenbotham, 144, West Street, Maritzburg, Natal; Arthur Edwin Tate, B.Sc., Gladstone House, Salter Row, Pontefract; Francis Lawry Usher, B.Sc., 18, Clifton Park, Bristol.

The selection by the Council of Professor F. S. Kipping, F.R.S., as Longstaff Medallist for 1909 was announced, the presentation to be made at the Annual General Meeting.

It was stated that the following changes in the Officers and Council were proposed by the Council:—

President to retire—Sir William Ramsay, K.C.B.

Vice-Presidents to retire—Dr. R. Messel and Prof. W. H. Perkin.

Ordinary Members of Council to retire—Dr. H. A. D. Jowett, Dr. F. E. Matthews, Dr. W. J. Sell, Dr. J. Wade.

As President—Prof. Harold B. Dixon.

As Vice-Presidents who have filled the office of President—Prof. H. E. Armstrong, Prof. A. Crum Brown, Sir William Crookes, Sir James Dewar, Dr. A. G. Vernon Harcourt, Prof. R. Meldola, Dr. H. Müller, Prof. W. Odling, Sir William Ramsay, Prof. J. Emerson Reynolds, Sir Henry E. Roscoe, Dr. W. J. Russell, Prof. T. E. Thorpe, and Prof. W. A. Tilden.

As Treasurer—Dr. Alexander Scott.

As Hon. Secretaries—Dr. M. O. Forster and Prof. Arthur W. Crossley.

As Foreign Secretary—Dr. Horace T. Brown.

As Vice-Presidents—Prof. J. Campbell Brown, Prof. J. N. Collie, Dr. J. J. Dobbie, Prof. F. S. Kipping, Sir A. Pedler, Prof. James Walker.

As New Ordinary Members of Council—Prof. W. A. Bone, Mr. C. E. Groves, Dr. G. T. Morgan, Dr. A. E. H. Tutton.

Dr. Arthur Harden, Dr. V. H. Veley, and Dr. J. A. Voelcker were elected Auditors to Audit the Society's Accounts.

A ballot for the election of Fellows was held, and the following were subsequently declared elected:—

George Henry Joseph Adlam, B.A.; Hubert Brunskill; Arthur Clayton, B.Sc.; Herbert Edwin Cocksedge, B.A., B.Sc.; Alfred Bertram Coles, M.A.; John Charles Jesser Coope; Frederick Percy Dunn, B.Sc.; Frederick Ferraboschi; John Thomas Fox; Arthur Gordon Francis, B.Sc.; John Thomas Funnell; Ross Aiken Gortner, M.A., B.Sc.; John Wilberforce Green; Alfred George Cooper Gwyer, B.Sc., Ph.D.; Robert Main Harland; Walter Norman Haworth, M.Sc.; Eric Hayward; Frank Higson; James Henry Hoseason; Ralph Hough; Robert Ernest Jackson; John Hugh Jeffery; Henry Humphreys Jones; Horace Keeble; Joseph Leedham; John Esson McGillvray, M.A.; William George Martin, B.Sc.; Percy May; William Norton Morley, B.Sc.; Frederick Hubert Painter, B.Sc.; Joseph Allen Pickard, B.Sc.; Frank George Pope; Colston James Regan; Robert Robinson, M.Sc.; Herbert Rogers; Philip John Sageman; J. H. Charles Schulten, Ph.D.; David Segaller; James Thomas Stevenson; Reginald Wells Varley; Guy Ransom Warwick, B.A.; Percy Charles Henry West; Thomas Jabez Wild.

Of the following papers, those marked * were read:—

*45. "A Study of some Asymmetric Compounds." By FREDERIC STANLEY KIPPING.

When a *dl*-acid is treated with a *d*-base, the product is a mixture of the *dAdB*- and *lAdB*-salts, and when a *d*-acid is combined with a *dl*-base, the components of the product are *dAdB* and *dAlB*. If therefore A and B represent a particular acid and a particular base respectively, and *dl*-A may be resolved with the aid of *d*-B, it might be inferred that *dl*-B could also be resolved with the aid of *d*-A. The *dAdB*-component is common to both original products, and as *lAdB* and *dAlB* are enantiomorphously related and have the same solubility in any given optically inactive solvent, the observed difference in solubility between *dAdB* and *lAdB* should also be effective in the case of *dAdB* and *dAlB*.

Now *dl*-sulphobenzylethylpropylsiliclyl oxide may be resolved with *d*- (or with *l*-) methylhydrindamine (*Trans.*, 1908, xciii., 457); experiments showed, however, that *dl*-methylhydrindamine could not be resolved with the aid of *d*-sulphobenzylethylpropylsiliclyl oxide under similar conditions.

dl-Methylhydrindamine may be resolved by fractionally crystallising its *d*-hydrogen tartrate from water (*Tattersall, Trans.*, 1904, lxxxv., 169); it is now shown that *dl*-tartaric acid may be resolved with *d*-methylhydrindamine under similar conditions, and that both the *dAdB*- and the *lAdB*-components may be isolated in one series of crystallisations.

dl-Hydrindamine cannot be resolved by fractionally crystallising its *d*-mandelate from water; *dl*-mandelic acid, however, is very easily resolved by fractionally crystallising from water its salt with *d*- (or with *l*-) hydrindamine.

These results seem to show that partly racemic molecules exist in solution.

DISCUSSION.

Mr. A. E. DUNSTAN agreed with Prof. Kipping that the physico-chemical evidence for the existence of racemic compounds in solution was slight, owing to the dissociation of these substances, but he pointed out that the results published by Clerk Ranken and Tayler, Stewart, Dunstan, and Thole, all indicated that undoubtedly there was a small difference between the physical properties of the racemic and the active compound when dissolved. Moreover, these differences were consistent and increased with the concentration.

*46. "The Decomposition and Sublimation of Ammonium Nitrite." By PRAFULLA CHANDRA RAY.

When an aqueous solution of ammonium nitrite is heated in a vacuum at about 37–40°, only a very small portion of the salt decomposes according to the equation— $\text{NH}_4\text{NO}_2 = 2\text{H}_2\text{O} + \text{N}_2$; the main bulk of the salt crystallising out. If the temperature is then gradually raised to 70°, slow decomposition continually proceeds according to the above equation, but the major portion sublimates un-

changed. When this sublimate is heated by means of a naked flame, the gaseous products are nitrogen and nitric oxide, the latter often amounting to as much as 6 per cent.

DISCUSSION.

Dr. DIVERS remarked on the interest attached to the crystallisation of ammonium nitrite from its aqueous solution and of the sublimation of a salt hitherto supposed to be too unstable for these operations to be possible. The generation of much nitric oxide when the sublimed salt was vaporised and further heated seemed to indicate the occurrence of a decomposition tending to that production of hydrazine which Professor Ray had looked for: $2\text{NH}_4\text{NO}_2 = \text{N}_2\text{H}_4 + 2\text{H}_2\text{O} + 2\text{NO}$, the elements of the hydrazine appearing as ammonia and nitrogen.

Dr. VELEY concurred with the author that ammonium nitrite in solution is best prepared by the decomposition of silver nitrite and ammonium chloride. It was a most interesting point that such a solution could be evaporated in a vacuum without decomposition, and that the ammonium nitrite could not only be crystallised out, but even purified by sublimation.

The observation was remarkable that if the conditions were such that the solid salt decomposed, then nitric oxide in a small proportion was formed in addition to nitrogen. Blanchard (*Zeit. Phys. Chem.*, 1902, xli., 681; and *Ibid.*, 1905, li., 117) had shown that when an aqueous solution containing potential ammonium nitrite is heated under atmospheric pressure, nitric oxide is formed in about the same proportion as that found by the author, but on reduction of pressure the proportion is reduced to nil. It would thus appear that the solid salt and aqueous solutions give the same result, although under reverse conditions.

*47. "The Estimation of Hydroxyl Derivatives in Mixtures of Organic Compounds." By HAROLD HIBBERT.

Hibbert and Sudborough's method (*Trans.*, 1904, lxxv., 933) for the estimation of hydroxyl groups in carbon compounds can be applied with equal success to mixtures of hydroxyl derivatives with other organic compounds, for example, ketones, esters, nitriles, &c. It is necessary to take rather more of the Grignard reagent than is sufficient to combine with both substances.

In this way the author has been able to estimate α -naphthol in presence of various ketones, ethyl benzoate, methyl hydrogen succinate, and acetonitrile, as well as chloral in a mixture of this with acetone.

*48. "A Simple Method for Determining the Chemical Affinity of Organic Substances." By HAROLD HIBBERT.

NOTE.—The author suggests using the term *affinergy* (compounded from *affin*-ity and *en*-ergy; German equivalent = *affinergie*) as a substitute for Michael's *chemical potential* (*Annalen*, 1908, ccclxiii., 21) in order to avoid confusion with the physical conception of potential (as in electrical potential), with which it has nothing in common.

The author has shown (preceding paper) that hydroxyl derivatives can be estimated in presence of ketones if excess of the Grignard reagent is employed. If now a quantity of the latter is taken, insufficient to combine with both, it is obvious that a partition of the reagent between the two substances will take place, and the amount of methane evolved will depend on their relative masses and reaction velocities, assuming, of course, that all the products (apart from the methane) remain in solution. The latter condition is fulfilled by working in phenetole solution. By taking the same hydroxyl compound, mixing it with equimolecular quantities of various ketones, and using the same (insufficient) amount of magnesium methyl iodide solution, it is thus possible to measure the relative reaction velocities of the ketones towards the reagent, since these are indirectly proportional to the amounts of methane evolved. The method serves in this way as a means for determining the chemical affinity of organic compounds.

The relative affinities (using α -naphthol) of the following

ketones have already been determined:—Dimethyl, methyl ethyl, and diethyl ketone; aceto- and benzo-phenone.

DISCUSSION.

Dr. LAPWORTH asked if the author had fully considered his assumption that velocity of the reaction in non-reversible changes might be taken as a measure of affinity. Scientists were agreed that changes could only occur spontaneously when a diminution in potential thereby resulted, but at present this principle, whilst often serving to indicate the direction of change in a chemical system, was difficult to develop for irreversible changes, and the determination of affinity seemed hardly satisfactory except in such cases where equilibrium conditions could be ascertained.

Dr. SENTER said that in his opinion the reactivity of a chemical system could best be expressed, with van't Hoff, by means of the equation:—

$$\text{Reaction Velocity} = \text{Driving Force/Resistance.}$$

The driving force was the "chemical affinity," and depended on the free energy of the system, which could be calculated, in a perfectly definite way, from equilibrium measurements. The reaction velocity might be enormously affected by slight changes in the medium or by catalysts, neither of which could, in general, modify to any great extent the free energy (or the chemical affinity). The fact that the free energy and the reaction velocity are affected so differently by reagents allowed to some extent of their investigation separately, and therefore this method of regarding the matter seemed to possess distinct advantages.

The PRESIDENT remarked that it is essential to distinguish between an energy and one of the factors of an energy:—

just as Heat Energy = Temperature $\times$ Entropy,
and as Electric Energy = Electric potential $\times$ Electric quantity,
so Chemical Energy = Chemical Affinity $\times$ Chemical quantity.

Now as chemical quantity is proportional to electric quantity (as is proved by Faraday's law), it follows that chemical and electric affinity must also be proportional. Therefore, by determining electric potential, chemical affinity is measured.

The word "affinergy" appears to be confusing, inasmuch as it combines the conception of a factor of an energy with the energy itself.

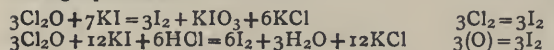
*49. "Chlorine Generated by Potassium Permanganate its Preparation and Purity." By EDGAR WEDEKIND and SAMUEL JUDD LEWIS.

The method of preparing chlorine by dropping concentrated hydrochloric acid on crystals of potassium permanganate, which was suggested by Graebe (*Ber.*, 1902, xxxv., 43), is stated to yield the gas free from oxides of chlorine, but no experimental proof of this is given by that author.

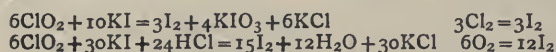
The purity of the gas has now, however, been ascertained by the following experiments:—1. On passing the gas through sulphuric acid no reddish coloration is produced, showing the absence of chlorine peroxide. (The formation of chlorine monoxide is improbable, as this would be at once decomposed by the hydrochloric acid). 2. 2.11 grms. of tin were heated to dull redness in a stream of the gas; the residue weighed only 0.7 mgrm. 3. The gas is completely absorbed by mercury. 4. A definite volume of the gas was absorbed by a solution of 15 grms. of potassium iodide in water, and the iodine liberated was titrated with sodium thiosulphate solution, of which 168.70 cc. (mean of four determinations) were required, whereas in a corresponding experiment with chlorine, generated from pure manganese dioxide and hydrochloric acid (and assumed to be free from oxides of chlorine, carbon dioxide, &c.), 168.67 cc. of thiosulphate solution (mean of six determinations) were used.

DISCUSSION.

Dr. SCOTT pointed out that, as potassium permanganate often contains small quantities of chlorate, chlorine prepared by its means is peculiarly liable to be contaminated with traces of chlorine oxides. The only safe test for the presence of these is to absorb the gas in a neutral solution of potassium iodide, and then decolorise it exactly by means of sodium thiosulphate; if, on adding to the colourless solution pure dilute hydrochloric acid, no iodine is liberated, then the chlorine may be regarded as quite free from its oxides, but any iodine liberated is exactly equivalent to the combined oxygen, since, in neutral solution, it goes to form iodate in accordance with the following equations:—



and—



Neither of the authors' assumptions (a) that hypochlorous anhydride must be absent, because of the presence of a large excess of hydrochloric acid, or (b) that chlorine peroxide could not be present, as the sulphuric acid by which the gas was dried did not acquire a reddish colour, was justified. What their experiments did prove was that the gas thus prepared was of the same order of purity as that from hydrochloric acid and manganese dioxide.

50. "The Isolation of the Aromatic Sulphinic Acids." By JOHN THOMAS.

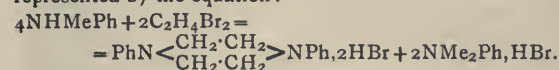
The aromatic sulphinic acids are characterised, as a class, by forming ferric salts which are insoluble in water and fairly concentrated mineral acids; this property can be usefully applied in the separation of these acids from the solutions in which they are produced. The ferric salts of benzenesulphinic, *o*- and *p*-toluenesulphinic, and α - and β -naphthalenesulphinic acids have been prepared and characterised, and simple methods indicated for converting them into the corresponding sulphinic acids, sulphonyl chlorides, and sulphonamides.

51. "Analytical Investigation of Zirconium Metal." By EDGAR WEDEKIND and SAMUEL JUDD LEWIS.

In view of zirconium having not yet been obtained in a pure condition, and of the lack of analytical data regarding the composition of the specimens obtained by various workers, the authors have worked out methods of analysis which make it possible to determine the proportions of the most common impurities. The zirconium existing in the free state is separated as the tetrachloride from that in combination with oxygen by burning the substance in pure chlorine; in this way the proportion of oxygen is determined directly. Nitrogen is estimated by a method similar to that of Kjeldahl; carbon by combustion of the metal in oxygen at very low pressure, and subsequent absorption of the carbon dioxide produced.

52. "The Action of Ethylene Dibromide on Monomethylaniline." By JOHN GUNNING MOORE DUNLOP and HUMPHREY OWEN JONES.

By the interaction of 2 grm.-molecules of monomethylaniline with 1 grm.-molecule of ethylene dibromide, diphenylpiperazine (m. p. 163°) is formed by a reaction represented by the equation:—



When 4 grm.-molecules of monomethylaniline are used instead of 2 in this interaction, diphenyldimethylethylenediamine, $\text{NMePh} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NMePh}$, melting at 47°, is produced.

53. "Salicylidene-*m*-toluidine, a New Phototropic Compound. Salicylideneamines: Salicylamides." By ALFRED SENIER and FREDERICK GEORGE SHEPHEARD.

In continuation of previous work on acridine synthesis, a series of new salicylideneamines and salicylamides have been prepared. Among these, *salicylidene-m*-toluidine has special interest, as it exhibits phototropy (Marckwald, *Zeit. Physik. Chem.*, 1899, xxx., 140). On crystallisation from its solutions, the crystals are pale yellow, but when exposed to sunlight the colour changes quickly to deep orange, and this colour change is reversed, although more slowly, when the crystals are placed in the dark. This reversible reaction is due to light waves of high refrangibility; it does not take place in solution, and the sensibility of the compound remains unimpaired after at least a month's time. No evidence could be obtained of triboluminescence or phosphorescence. Salicylidene-*m*-toluidine behaves in this respect like the anhydrous chloride of quinoquinoline and β -tetrachloro- α -ketonaphthalene studied by Marckwald. It is similar also to the fulgenic acid compounds investigated by Stobbe (*Annalen*, 1908, ccclix., 1). Probably phototropy in this instance, as is supposed to be the case in others, depends on the existence of two stereo- or other isomerides formed respectively under the influence of short or long waves of light.

54. "The Action of Ethyl Carbamate on Esters of Organic Acids and Mustard Oils." By SIEGFRIED RUHEMANN and JOHN GILLIES PRIESTLEY.

Ethyl phenylpropionate does not form an additive product with ethyl sodiocarbamate, but condenses with it to yield ethyl phenylpropionylcarbamate, $\text{C}_6\text{H}_5\text{C}:\text{C} \cdot \text{CO} \cdot \text{NH} \cdot \text{CO}_2\text{Et}$. This reaction has been applied to the preparation of acyl derivatives of ethyl carbamate from esters of fatty and fatty-aromatic acids. In this way, also, ethyl formylcarbamate, $\text{CHO} \cdot \text{NH} \cdot \text{CO}_2\text{Et}$, has been obtained, which is readily hydrolysed by mineral acids, even in the cold.

The esters of benzenecarboxylic acids form either only very small quantities of the acyl derivatives of ethyl carbamate as with ethyl benzoate, or no trace of the acyl carbamate, as with ethyl *o*-phthalate.

Phenylthiocarbimide reacts with ethyl sodiocarbamate to form carboxyethylphenylthiocarbimide, $\text{NH}(\text{CO}_2\text{Et}) \cdot \text{CS} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$ (see Doran, *Trans.*, 1896, lxix., 326), and a yellow compound having the formula $\text{C}_6\text{H}_5 \cdot \text{NH} \cdot \text{CS} \cdot \text{N} = \text{CO}$

$\text{C}_6\text{H}_5 \cdot \text{N} = \text{C} = \text{S}$, which is anhydro-diphenyldithiobiurettcarboxylic acid. It forms colourless sodium and potassium salts, and is readily decomposed by alkalis. Alkali-thiocarbimide yields with ethyl sodiocarbamate a substance, $\text{C}_9\text{H}_{11}\text{ON}_3\text{S}_2$, with similar properties to those of the former compound.

55. "The Hydrolysis of Amygdalin by Emulsin. Part III. Synthesis of *d*-Benzaldehyde-cyanohydrin." By SAMUEL JAMES MANSON AULD.

The assumption generally made that benzaldehyde-cyanohydrin must be formed as an intermediate product of the decomposition of amygdalin by emulsin is objected to, and evidence has been brought forward showing that an asymmetric synthesis of *d*-benzaldehyde-cyanohydrin takes place under the influence of emulsin, and that its formation in this manner proceeds more rapidly than its formation during the hydrolysis of amygdalin by emulsin. Emulsin can also induce the formation of an optically active hydroxybenzaldehyde-cyanohydrin from hydroxybenzaldehyde and hydrocyanic acid.

Royal Institution.—On Thursday next, March 11, at 3 o'clock, Mr. A. D. Hall, Director of the Rothamsted Experimental Station, begins a course of two lectures at the Royal Institution on "Recent Advances in Agricultural Science." The Friday Evening Discourse on March 12 will be delivered by Mr. S. G. Brown, on "Modern Submarine Telegraphy"; and on March 19 by Mr. R. Threlfall, on "Experiments at High Temperatures and Pressures."

NOTICES OF BOOKS.

The Chemical Constitution of the Proteins. By R. H. ADERS PLIMMER, D.Sc. Parts I. and II. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1908.

IN this monograph a full account is given of the present state of our knowledge of the chemistry of the proteins, and as the vast amount of material which could not be left unnoticed would have made the monograph exceed the prescribed size of the series, it was divided into two parts. In the first methods of investigating the proteins are treated historically, the isolation of the amino acids and the chemistry of the units of which the protein molecule is built up are discussed. The second part deals with the synthesis of the proteins, and describes fully Fischer's masterly work on the polypeptides. This difficult subject is made admirably clear and interesting, and is brought down to the latest possible date.

An Intermediate Course of Laboratory Work in Chemistry. By EDWARD KENNETH HANSON, M.A. (Cantab), F.I.C., and JOHN WALLIS DODGSON, B.Sc.(Lond.). London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1908.

A STUDENT who is attending fairly advanced lectures on inorganic chemistry will find that this laboratory book describes a very suitable course of practical work to accompany them. It gives first methods of preparing various inorganic compounds. Full directions are included for the experimental work, which sometimes requires a good deal of manipulative skill, and illustrations of the more complicated apparatus are provided. The substances treated include the less common compounds, which would not have been studied in an elementary course of practical chemistry, and some additional problems are suggested for solution. Volumetric work is treated from the commencement, and some moderately difficult estimations are described, besides the usual acid and alkali and oxidation titrations. The section on gravimetric work gives the typical methods of estimation. The solubility of salts in water would most probably have been studied in a preliminary course, and it would perhaps have been advisable to omit the section on this subject and give additional room to the consideration of spectroscopic analysis. Finally, the qualitative analysis of simple substances is treated in outline on a novel plan. The student is told what substances to use as group reagents and what confirmatory tests to adopt, but in every case he is not told the result of the test but is left to construct tables for himself with his own laboratory notes to go upon. Thus much haphazard work is avoided, and also there is no chance of the qualitative analysis degenerating into blind compliance with certain directions which lead to previously explained results.

Essays, Biographical and Chemical. By Sir WILLIAM RAMSAY, K.C.B. London: Archibald Constable and Co., Ltd. 1908.

THE essays in this book have either been delivered as lectures or published as articles in magazines during the last twenty-five years, and it is easy to foretell that their publication in book form will bring genuine pleasure to many students of chemistry. The style in which they are written is delightful, and although the essays on chemical and allied subjects in the second part are in a certain sense popular and not intended to appeal to a specially trained class of readers, they are by no means superficial. The last essay on the functions of a university must prove inspiring to the most phlegmatic, and all teachers, even of elementary classes, will learn valuable lessons from it as to what should be the aim of all scientific instruction. The earlier essays deal with the history of chemistry and relate to

various periods, all of which are treated with the same insight and illuminative descriptive power. The essay on the early days of chemistry deals with the knowledge of the ancients, and that on the great London chemists with the special claims to renown—Boyle, Cavendish, Davy, and others. Of more recent heroes of science one essay discusses the life and work of Lord Kelvin, and another has for its subject Berthelot; both are marked by a whole-hearted and generous recognition of the great qualities of these two famous men, and of the immense value of the results of their labours which were given to the world.

The Toil of Life. By FRANCIS STOPFORD. Second Edition. London and Felling-on-Tyne: The Walter Scott Publishing Co., Ltd. 1908.

THIS is a book which undoubtedly contains a message for the toilers of the earth, to whom it is dedicated, and every thinking person will find profit in pondering over its theories. The author's simple straightforward philosophy is refreshing and at the same time stimulating, and there is a charm about the book which is irresistible. A preface has been added to the second edition, explaining what was the source and inspiration of the original, and giving a further insight into the author's exalted views on the meaning of life.

The Chemical Analysis of Iron. By ANDREW ALEXANDER BLAIR. Seventh Edition. Philadelphia and London: J. B. Lippincott Company. 1908.

THE alterations made in the seventh edition of this standard work on the analysis of iron are comparatively trifling, but at the same time they all make for the greater efficiency and value of the book. New methods of separating vanadium, molybdenum, chromium, and nickel in steel, which have been worked out recently, are now included. In the case of vanadium the author recommends Campagne's method as being simple, accurate, and rapid. Also the volumetric method of determining nickel by titration with a standard solution of potassium cyanide, which has been found to give very satisfactory results, is described. The atomic weights throughout the book have been altered in accordance with the report of the International Commission for 1908, and all factors have been recalculated when necessary.

Photographic Optics and Colour Photography. By GEORGE LINDSAY JOHNSON, M.A., M.D., B.S., F.R.C.S. London: Ward and Co. 1909.

AN excellent treatment of both the practical and theoretical side of optics is given in this book, every page of which shows that its author has a special knowledge of the subject. It opens with a description of the various kinds of cameras, explaining the working of different types, and the special merits of each, and here the author's experience of the instruments of different makers enables him to give valuable advice on practical details. The lens is next considered, and in these chapters the mathematics introduced are simplified as far as possible, and practical problems are illustrated by simple examples which are worked out in full; these typical examples have been carefully chosen to include all kinds of problems, and are explained remarkably clearly. Methods of testing lenses and their use for magnifying and reducing, and many special problems in photography are next considered, such as the measurement of the speed of a shutter. Finally, a very lucid account is given of the present state of colour photography, in which the different processes are explained in language which cannot fail to be understood. Excellent reproductions are given of photographs in colour, and for this part alone the book is well worth procuring and reading. The author's hints on photography, on the management of the plate and its development, will be appreciated by the amateur, and even the professional

cannot afford to ignore the valuable suggestions which are scattered through the book, which is a thoroughly modern text-book on applied optics.

Die Elektrischen Eigenschaften und die Bedeutung des Selen für die Elektrotechnik. ("The Electrical Properties and Importance of Selenium in Electro-technics"). By Dr. CHR. RIES. Berlin: Administration der Fachzeitschrift "Der Mechaniker." 1908.

THE properties of selenium, which are particularly interesting both from a scientific and technical point of view, are exhaustively treated in this monograph, which gives an excellent summary of all that is at present known of the element. The preparation of selenium cells is discussed in the early part of the book, and the influence of temperature upon electrical conductivity is treated fully. The importance of selenium in electro-technics is constantly emphasised, and many graphical representations of the variations in its sensitiveness to light, conductivity, &c., are reproduced in order to make the subject clear. A summary of the literature of selenium includes all important books and articles which have been published dealing with its physical or chemical properties, and has been brought down to the year 1908.

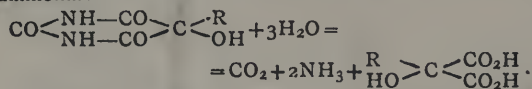
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlviii., No. 4, January 25, 1909.

New Method of Preparing Alcoholic Oxides.—J. B. Senderens.—Alumina obtained by precipitating sodium aluminate with sulphuric acid dehydrates alcohols, giving alcoholic oxides. At 200° alumina begins to decompose ethyl oxide, and it yields large quantities of ethylene at 300°. If the temperature is kept below that at which the ethyl oxide is destroyed, the latter can readily be obtained by condensing the products of the reaction and allowing the liquid obtained to stand for some time. Thus two layers of liquid are obtained, the lower being water containing about one-tenth of its volume of ethyl oxide, and the upper ethyl oxide containing a very small quantity of water.

Condensation of Mesoxalic Ethers with Tertiary Aromatic Amines.—A. Guyot and E. Michel.—Aromatic amines combine with alloxan without elimination of water, the general formula of the products being $\text{CO} \begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix} \text{CO} \begin{smallmatrix} \text{C} \\ \text{C} \end{smallmatrix} \begin{smallmatrix} \text{R} \\ \text{OH} \end{smallmatrix}$; where R is phenyl, naphthyl, &c. Under the action of aqueous alkalis these products split up into substituted tartronic acids, carbon dioxide, and ammonia:—



These tartronic acids, when treated with hot concentrated sulphuric acid give the corresponding aldehydes quantitatively, $\text{R}-\text{COH}(\text{CO}_2\text{H})_2 = \text{R}-\text{COH} + \text{CO}_2 + \text{CO} + \text{H}_2\text{O}$. With oxidising agents they give glyoxylic acids, and when heated alone or in aqueous solution they give up carbon dioxide, yielding glycollic acids, $\text{R}-\text{COH}(\text{CO}_2\text{H})_2 = \text{CO}_2 + \text{R}.\text{CHOH}.\text{CO}_2\text{H}$.

No. 5, February 1, 1909.

New Reactions of Dioxycetone.—G. Denigès.—When dioxycetone is prepared from glycerin by the

action of bromine, it gives certain colour reactions which are very characteristic, if it is not separated from the medium in which it has been formed. Thus, a strawberry-red coloration is obtained with salicylic acid, and a dark violet with gallic acid. These reactions are not due to glyceric acid, the corresponding aldehyde, nor to glycerin itself, but are produced by the bromine set free by the action of concentrated sulphuric acid on hydrobromic acid mixed with dioxycetone, and derived from the action of the halogen on the glycerin.

Action of Air and Oxidising Agents on Coal.—O. Boudouard.—The author has determined the change of weight of various specimens of coal when subjected to the action of air at different temperatures, also to the action of nitric acid, and has found that the increase of weight observed is due to the absorption of oxygen. The phenomenon is more noticeable when the temperature is raised. Coking coals when oxidised at 100° completely lose their coking power, and, moreover, they then contain humic acid which was not present previously. A more energetic oxidising agent such as nitric acid gives a larger proportion of humic acid.

Formation of Hydrocyanic Acid by the Action of Nitric Acid on Phenols and Quinones.—A. Seyewitz and L. Poizat.—Twenty per cent nitric acid when boiling oxidises many aromatic compounds, setting free hydrocyanic acid. This action takes place only in presence of a phenol or quinone group, and it is only those compounds which have the para-position free, or the two ortho-positions free, which liberate HCN. Nitrous acid is also always formed, and substances which destroy nitrous acid, e.g., urea or aniline, stop the formation of hydrocyanic acid. The nitrous acid first yields a para- or ortho-nitroso-derivative, and then oxidation occurs at the double bond, and mesoxalic acid and the oxime of the acid are formed, or else carbon dioxide, oxalic acid, and the monoxime of dioxytartaric acid. The mesoxalic or oxalic acids then give up carbon dioxide, and the oxime condenses, evolving hydrocyanic acid.

Action of Nitrosobenzene upon Secondary Amines.—P. Freundler and M. Juillard.—Nitrosobenzene reacts energetically with secondary amines, being transformed chiefly into azobenzene. Some nitrobenzene, aniline, and probably a little azoxybenzene are also formed. The greater part of the amine remains unaltered. Under certain conditions a secondary hydroxylamine, $\text{RR}'\text{NOH}$, is formed. The authors have observed that isoamylamine is soluble in water in all proportions. Methylisoamylamine is hardly soluble, but if to equal volumes of the secondary base and water one-fourth or one-fifth of primary amylamine is added, the mass becomes homogeneous. If the mixture is heated to 50° the secondary base separates completely, taking with it most of the primary amine. The authors think that methylisoamylamine forms a hydrate soluble in aqueous solutions of the primary base. This hydrate, which loses its water on heating and becomes insoluble, undoubtedly exists, for methylisoamylamine absorbs water with a rise of temperature, and when the homogeneous liquid thus obtained is heated water again separates.

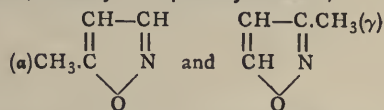
Reactions of the 9.10 Dihydride of Anthracene and of Anthranol.—R. Padova.—When heated with sulphur to 200° the dihydride of anthracene gives anthracene. It does not condense with aromatic aldehydes, and does not react with benzylidene chloride nor with phenyl chloroform in xylene. When it is heated with phenyl chloroform and powdered marble, resinous products are obtained. Anthracene dihydride condenses with benzophenone chloride, giving tetraphenylanthraxylidene. Chloroform and alcohol potash give a red crystalline substance, the analysis of which shows that it is 10-oxanthryl-9-anthraquinone methane.

Berichte der Deutschen Chemischen Gesellschaft.

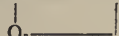
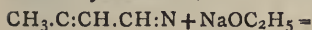
Vol. xlii., No. 1, 1909.

Selenous Mercaptans and some of their Derivatives.—L. Tschugaeff.—To prepare selenous mercaptans, sodium hydroselenide solution is treated with the bromide or iodide of an alcohol radical in an atmosphere of hydrogen; the liquid is heated on the water-bath, poured into water, and the oil which separates is shaken with caustic soda solution, when the mercaptans formed go into solution. They may be set free by acetic acid. The selenous mercaptans are heavy colourless liquids which react with mercury oxide, and give characteristic coloured precipitates with all salts of the heavy metals in aqueous or alcoholic solution, the orange precipitates with lead and thallous salts being specially characteristic. The selenous mercaptans are autoxidisable substances, giving diselenides in air. $2C_2H_5SeH + O_2 = C_2H_5Se_2C_2H_5 + H_2O$. They react with magnesium methyl iodide as follows:— $RSeH + CH_3MgI = RSeMgI + CH_4$. Selenides of formula R_1SeR_2 can be prepared by treating mercaptans in absolute alcohol with sodium alcoholate, and then adding the bromide or iodide of the corresponding alcohol radical. Diselenides of general formula $RSe(CH_2)_nSeR$ result from the action of the dibromides, $Br(CH_2)_nBr$, on the sodium derivatives of selenous mercaptans, $2NaSeR + Br(CH_2)_nBr = RSe(CH_2)_nSeR + 2NaBr$.

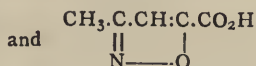
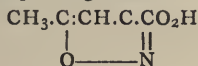
α -Methylisoxazol.—L. Claisen.—When hydroxylamine acts on oxymethylene acetone, methylisoxamine is formed, $C_4H_6O_2 + NH_2OH = C_4H_5NO + 2H_2O$. The product, however, is not a single substance but a mixture of two isomers, α -methyl and γ -methylisoxazol,—



The α -derivative boils at 122° and the γ -derivative at 118° . The former is converted by alcoholic sodium ethylate into sodium cyanacetone,—



and the latter yields acetic acid and acetonitrile. The two corresponding acids,—



have been prepared. The compound obtained by Schmidt and Widmann from diacetosuccinic acid ester, and thought by them to be isoxazol, has undoubtedly not the composition they ascribe to it, nor does it appear to be cyanacetone.

Polymerisation as a cause of the Difference of Colour of Haloid Salts and Sulphites.—A. Hantzsch.—Many inorganic haloid salts are more or less strongly coloured, while the corresponding salts of strong oxyacids, e.g., nitrates, chlorates, sulphates, perchlorates, &c., are colourless. The same phenomenon is observed with some organic salts, and is specially marked with the acridine bases. The explanation based upon the auxochrom theory is not satisfactory, and the author ascribes the differences of colour to a chemical cause, namely, polymerisation. He has not as yet deduced specific relations between the constitution of salts and their power of forming dark coloured polymers, but it may be stated generally that polymerisation occurs more readily the more unsaturated the cation is and the more loosely the anion and cation are bound together.

Volatility of Arsenic and Thallium in vacuo. Method of Calculating the Boiling-point of Metals.—F. Krafft and A. Knocke.—A specimen of arsenic kept

in vacuo for twenty-four hours at room temperature showed no loss of weight. Hence, arsenic is not volatile at the ordinary temperature. Volatilisation begins in a vacuum at 96° and rapid sublimation at 325° . At a temperature of 554 — 556° arsenic sublimates under a pressure of 760 mm., and when these data are compared the following result is obtained:—

Incipient volatilisation, 0 mm.	96°	} Difference 229°
Sublimation, 0 mm.	325°	
Sublimation, 760 mm.	554°	} Difference 229°

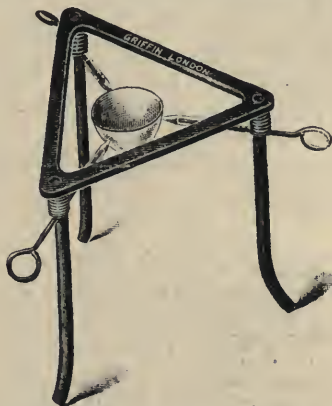
For any metal given any two of these constants, the third can be calculated. In the case of thallium, evaporation begins under 0 mm. at 174° , and the boiling-point under 0 mm. is 818° . The difference, 644° , added to 818° , gives the boiling-point under 760 mm., viz., 1462° .

Evaporation of Non-volatile Metals, especially Platinum and Iron, in Evacuated Glass Vessels.—A. Knocke.—The least volatile metals can be volatilised in vacuo at comparatively low temperatures in glass vessels. Experiments with the metals of the alkaline earths show that strontium is somewhat more volatile than calcium, and barium, which has the highest atomic weight, is also the most volatile of the three alkaline earth metals. Platinum volatilises rapidly in a vacuum at 700° and palladium at 735° . Of the metals of the iron group, cobalt, with higher atomic weight, evaporates much more easily than iron, and nickel lies between the two metals in this respect.

Colloidal Potassium Chloride.—C. Paal and Kurt Zahn.—The solid organosols of potassium chloride, prepared either by precipitation from their colloidal solutions, or directly, and the KCl gels, like the corresponding sodium salts, are adsorption compounds. These adsorption compounds of potassium chloride exist in five different modifications, solid and liquid organosol, liquid gel, solid reversible gel soluble in benzene, and solid irreversible gel. These modifications can be prepared in the same way as the corresponding compounds of sodium chloride.

MISCELLANEOUS.

The Universal Crucible Support.—(Designed by G. T. HOLLOWAY, and made by J. J. GRIFFIN and SONS, Ltd.)—The device consists of a set of three sliding rods pointed with quartz. The rods pass obliquely through the legs of a suitable tripod, and are held firmly in their correct positions by the action of strong brass springs. They may



be adjusted to support crucibles and vessels of any shape or material with the greatest ease. The little pointed caps are made of pure silica, and do not break the flame. They are of course incorrodible in the ordinary sense of the word,

and may therefore be safely used with platinum crucibles. There being only three points of contact, the contents of the crucibles are heated uniformly, and there is no necessity to turn the crucible round to complete an ignition, as must be done when using an ordinary pipeclay triangle. The support is practically indestructible, and should find a



place in every laboratory. The three silica points will enclose a circle 3 in. diameter. For use with quartz crucibles and capsules it is incomparable. This combined apparatus is always ready. It is less costly than a tripod and platinum triangle combined, and its reliability and convenience are obvious.

Fresenius Chemical Laboratory in Wiesbaden.—Vacation Courses have been recently established; the first of these was given in the autumn of 1908; the students numbered 10. During the current Winter Term, 1908-1909, the laboratory was attended by 27 students, among whom was 1 lady. Of these, 12 were from the German Empire, 3 from Austria-Hungary, 3 from the United States of North America, 2 from England, and 1 each from Switzerland, Luxemburg, Belgium, Norway, Russia, East India, and Japan. In addition to the directors, Geheimer Regierungsrat, Prof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, and Prof. Dr. E. Hintz, there are five teachers and heads of departments, two assistants in the Instruction Laboratories, and twenty-two assistants in the private laboratories. The next Summer Term begins on April 26th of this year. During the Winter Term a number of scientific researches were published from the Laboratory. The various articles appeared in the chemical periodicals, especially in the *Zeitschrift für Analytische Chemie*, which is edited by the directors of the Laboratory. In addition to the scientific researches during the Winter Term of 1908-1909, numerous analyses were made in the different departments of the Laboratory in the interest of trade, mining, industry, agriculture, hygiene, justice, and government.

MEETINGS FOR THE WEEK.

- MONDAY, 8th.—Royal Society of Arts, 8. (Cantor Lecture). "Modern Methods of Artificial Illumination," by Leon Gaster.
- TUESDAY, 9th.—Royal Institution, 3. "Evolution of the Brain as an Organ of Mind," by Prof. F. W. Mott, F.R.S.
- WEDNESDAY, 10th.—Royal Society of Arts, 8. "Application of the Microscope to the Study of Metals," by Walter Rosenhain.
- THURSDAY, 11th.—Royal Institution, 3. "Recent Advances in Agricultural Science," by A. D. Hall, M.A.
- FRIDAY, 12th.—Royal Institution, 9. "Modern Submarine Telegraphy," by Sidney G. Brown, M.I.E.E.
- Physical, 8. "Effect of Radiations on the Brush Discharge," by A. E. Garrett. "On Pirani's Method of Measuring the Self-inductance of a Coil," by E. C. Snow. Exhibition of a High Potential

Primary Battery, by W. S. Tucker. "On the Least Moment of Inertia of an Angle Bar Section," by H. S. Rowell.

SATURDAY, 13th.—Royal Institution, 3. "Properties of Matter," by Prof. Sir J. J. Thomson, F.R.S.

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THE CHEMICAL NEWS.

VOL XCIX., No. 2572.

THE ISOLATION AND SYNTHESIS OF UREA.

By F. D. CHATTAWAY, F.R.S.

AMONG the almost bewildering number of compounds known to chemists there are few, if any, which surpass urea in interest.

This is obvious whether one considers the part it has played in the development of organic chemistry and the number of well-known compounds which can be made from it, or the circumstance that it is the form in which nitrogen is mainly excreted.

There is no animal matter which has been subjected to a more rigorous examination than urine, and it is somewhat of a surprise to find that urea, which is its most important constituent, was not properly isolated till the close of the eighteenth century. During the preceding century, chemists from the time of Boerhaave (1668—1738) to that of Scheele (1742—1786) almost exclusively occupied themselves with the phosphates which are contained in it. This great attention to the phosphates arose from the interest inspired by the discovery of phosphorus, which was obtained originally by strongly heating with white sand the residue left after evaporating urine. Scheele even failed to notice the presence of urea in urine. He, however, was chiefly concerned with the uric acid contained in it. It is worth noting that it is not necessarily the substance present in largest amount in any natural product which is first discovered, but the one which is most easily isolated, and hence generally the insoluble or least soluble part.

Urea appears to have been noticed first in 1773 by Rouelle* the younger, and styled the "saponaceous extract of urine." It was, however, first definitely isolated by Fourcroy (1755—1809) and Vauquelin (1763—1829), who in 1799 and 1800 published two memoirs upon the constituents of urine (*Annales de Chimie*, 1799, xxxi., 49; 1800, xxxii., 80). They state that, although they have searched through the works of all authors who have written upon urine, they cannot find any precise information which could refer to this body before 1773.

Boerhaave, of Leyden, in speaking of the evaporated residue, states that it resembles honey in appearance, but Rouelle was the first to make any express mention of a distinct substance and to give a few of its characters, publishing his observations in November, 1773, in the *Journal de Medecin*.

Fourcroy and Vauquelin obtained urea in a state of comparative purity by evaporating urine and extracting the syrupy residue by alcohol. The alcohol was distilled off, and the solution left to cool, when crystals separated; these were purified by repeated crystallisation from water, or better from alcohol. They recognised their product as a definite new compound, and described many of its more obvious properties. They gave it the name of "urée," which they say connects it in the mind with urine from which they had obtained it.

During the next twenty years urea was prepared by a number of chemists, but evidently their methods still left something to be desired, for Dr. William Prout, in 1818, devised an improved process. His paper was published in the eighth volume of the *Med. Chir. Transactions*, and the part dealing with urea is reprinted in Thomson's "Annals of Philosophy," 1818, xi., 352.

He obtained urea by evaporating urine to the consistency of syrup and adding nitric acid till the whole was converted into a crystalline mass. This was washed slightly with cold water, and the nitric acid then neutralised by a solution of potassium or sodium carbonate. The greater part of the potassium or sodium nitrate was then removed by crystallisation, the mother-liquor was made into a paste with animal charcoal, and the urea dissolved out from this by cold water. This aqueous solution was next evaporated to dryness and the urea extracted by alcohol. To obtain it perfectly pure it was necessary to re-crystallise it several times from alcohol. Having thus prepared pure urea Prout described its properties very carefully and analysed it. He does not give any details of the method used, but says "The substance under examination was heated with oxide of copper in an apparatus so contrived that the amount of water and carbonic acid formed might be accurately ascertained and the carbon and hydrogen thus estimated while the azote remained uncombined."

The accuracy of his results, considering the time at which the analysis was made, is remarkable. He determined the percentage composition to be—H = 6.66, C = 19.99, N = 46.66, O (by difference) 26.66; the percentage composition calculated from the formula, using the most recent international atomic weights, being—H = 6.71, C = 19.96, N = 46.71, O = 26.62.

Some years later large quantities of urea were required in the hospital of St. Antoine in Paris for making experiments (which were unsuccessful) as to its efficacy as a therapeutic agent in cases of diabetes, and M. Henry, who was charged with making it in the Central Pharmacy of the Civil Hospitals of Paris, devised a somewhat less troublesome method of obtaining it in quantity (*Journal de Pharmacie*, 1829, xv., 161).

Henry suggested that a slight excess of subacetate of lead or hydrate of lead, either of which precipitates the acids of the salts contained in it and much of the mucous and animal matter, should be added to fresh urine. The precipitate having been filtered off and any dissolved lead removed by adding dilute sulphuric acid, the liquid was concentrated, animal charcoal being added during ebullition, and filtered; the filtrate was then further evaporated till crystals separated; these were mixed with a little dry sodium carbonate and the urea extracted by alcohol. The product was finally re-crystallised from water.

This practically concludes the important work on the preparation of urea from urine, the problem having been to separate it from the uric acid, phosphates, and animal matters contained in this fluid. It is still always prepared by processes not essentially differing from those of Prout and Henry, either by removing the urea from the concentrated urine as a sparingly soluble salt such as the nitrate or oxalate, the other constituents remaining behind in the mother-liquor, or by precipitating the other constituents by oxide of lead, thus leaving the urea and little else in the filtrate.

This carries the history of the compound to the period of one of those great discoveries which from time to time alter the whole outlook of chemistry. Organic chemistry dates from it in two senses; it broke down the barrier between organic and inorganic chemistry, and was the first example of organic synthesis.

At this time, 1828, a very large number of well-defined substances obtained from animal and vegetable sources had become thoroughly well known; they had been analysed and the fact established that in spite of a great diversity in properties they were composed of a very few elements. The more these substances were studied the more evident it became that they possessed no peculiar characteristics which distinguished them from compounds of mineral origin; they had the same constancy of composition as inorganic compounds, and their constituent elements were present in the proportions required by their atomic weights. Almost all chemical and physical properties were common to both classes; only in one particular did substances of

* Hilaire Marin Rouelle (1718—1779), brother of the more celebrated Guillaume Francois Rouelle (1703—1770) who was one of the most eminent of the French chemists of the eighteenth century, and the teacher of Lavoisier.

animal or vegetable origin differ from substances obtained from non-organic sources—they could not be built up from their constituent elements in the way most inorganic substances could.

This is, however, such a fundamental difference that one is not surprised that many chemists of the time thought that these bodies must be elaborated in animals and plants under conditions which could not be realised outside such living organisms. The processes by which they were formed appeared so mysterious that a peculiar force, the "vital force" or "lebenskraft" was called into existence to explain them. It is difficult to trace the origin of this conception; it probably arose from the idea that some particular substance active only during life was common to all living matter, and that this living material was necessary to the formation of all organic compounds.

The idea that there exists an essential difference in nature between organic and inorganic compounds was shown to be untenable when Wöhler effected the synthesis of urea. This discovery so changed the direction of chemical thought and opened up such wide possibilities that the paper in which it is described, in spite of its confused style and frequent repetition, takes rank as one of the most notable ever written. It was published in 1828 in Poggendorf's *Annalen der Physik und Chemie*, 1828, xii., 253, under the title "Ueber Künstliche Bildung des Harnstoffs," and no apology is needed for quoting from it a free rendering of Wöhler's own words:—

"A crystalline white substance . . . is invariably obtained whenever one attempts, for example, by so-called double decomposition to combine cyanic acid with ammonia. The circumstance that on combination these substances appear to alter their nature and that a new compound results has turned afresh my attention to the subject. The investigation has led to the unexpected conclusion that urea is formed by the union of cyanic acid and ammonia. This observation is especially noteworthy, as it affords an example of the artificial production of an organic and indeed of a so-called animal substance from inorganic material. I have further noticed that the above mentioned white crystalline body is best obtained either by decomposing cyanate of silver by a solution of sal-ammoniac or lead cyanate by liquid ammonia. I prepared the considerable quantity required for its investigation in the latter manner. I thus obtained it in clear colourless crystals often more than an inch long, which formed slender rectangular four-sided prisms without definitely pointed ends. When this substance was heated with potash or with lime no trace of ammonia was liberated. With acids it did not show the characteristic behaviour of cyanates which when thus treated yield carbonic and cyanic acids. Further, it did not, as true salts of cyanic acid do, give a precipitate with salts of silver and lead. It could, therefore, contain neither cyanic acid nor ammonia as such.

"As I found that in the last named method of preparation nothing was formed beside it except pure lead oxide, I drew the conclusion that by the union of cyanic acid and ammonia an organic substance was produced perhaps similar in nature to the vegetable salt-forming bases. With this idea in my mind, therefore, I set on foot an investigation into the behaviour of the crystalline body towards acids. It, however, showed itself indifferent to these except to nitric acid, which when added to a concentrated solution at once produced a precipitate consisting of glittering scales. These after being purified by frequent re-crystallisation showed such a marked acid character that I was inclined to regard them as a peculiar acid when I found that on neutralising them by bases they yielded salts of nitric acid from which the crystalline material in question could again be extracted by alcohol, with all the characteristics it possessed before being acted upon by the nitric acid. This behaviour, so strikingly similar to that of urea, induced me to compare it with perfectly pure urea separated from urine. This comparison established beyond doubt that the crystalline body or cyanate of ammonia, if

one may call it so, and urea are one and the same substance."

He adds in conclusion, "I refrain from putting forward here the reflections which naturally present themselves as a consequence of the fact here established that compounds of the same elements having the same composition may possess very different properties."

Berzelius, referring to Wöhler's discovery in the ninth issue of the *Jahresbericht*, is much clearer. He states:—"One of the most unexpected, and on that account most interesting, of recent discoveries in the department of animal chemistry is incontestably Wöhler's artificial production of urea. This chemist finds that when silver cyanate is treated with a solution of ammonium chloride or lead cyanate with ammonia, a crystalline substance is formed, which possesses to the slightest detail all the properties of pure urea, and is, in fact, urea itself. Urea, however, is not on that account to be regarded as ammonium cyanate; the elements are united in it in a different way, so that the strongest bases can no longer liberate ammonia from it, nor the strongest acids set free cyanic acid. One can only say that this substance has changed from a compound inorganic atom of the second order to a compound organic atom of the first order. This fact affords a key to many difficulties, and shows that the same number of simple atoms distributed among themselves in dissimilar ways in compound atoms can give rise to bodies with different properties."

The course of the reaction which takes place when ammonium cyanate passes into urea has never been explained. Liebig and Wöhler later showed that the reverse change could be effected, and that when urea is mixed with an aqueous solution of AgNO_3 and evaporated to dryness, it is completely resolved into ammonium nitrate and cyanate of silver. Walker has recently shown that the transformation of ammonium cyanate into urea is a reversible action, and that equilibrium is reached at 100° when about 5 per cent of the urea is changed.

Although the fact that urea is easily broken down into carbon dioxide and ammonia when heated with acids or with alkalis led chemists, as soon as molecular structure began to be considered, to regard it as the amide of carbonic acid, this view was not supported by any direct synthesis of the compound from derivatives of the acid until Natanson, nearly thirty years after Wöhler's work, obtained it by the interaction both of the chloride and of the ethyl ester of carbonic acid with ammonia.

Natanson in his paper ("Ueber zwei Künstliche Bildungsweisen des Harnstoffs," *Ann.*, 1856, xcvi., 287) describes his experiments as follows:—"If ethyl carbonate is heated with ammonia in a sealed tube at 100° urethane only is formed, but if the temperature is raised to about 180° , the latter through the action of the excess of ammonia is converted into urea. In the part of the tube not filled by the liquid, a sublimate of undecomposed urethane is formed, while the aqueous solution contains the urea. When this solution is evaporated to dryness and the residue heated for some time to 100° , most of the urethane remaining volatilises, and urea, which can be immediately recognised by its reaction with nitric acid, remains behind." Completely to remove the last traces of urethane the urea was washed with ether, in which the former compound is easily soluble. The urea thus obtained was analysed and compared with natural urea, with which it was found to correspond in every respect.

Much earlier, Regnault (*Ann. Chim. Phys.*, 1838, lxi., 180) had investigated the white neutral substance produced when dry phosgene and ammonia are brought together, and had shown that it behaved in some of its reactions as a mixture of sal-ammoniac and the amide of carbonic acid. He, however, concluded that the carbamide which he believed to be present was not identical with urea, since, on adding strong nitric acid to a saturated solution of the white mixture, nothing separated, while urea nitrate was at once precipitated on similarly treating a solution of urea.

Natanson re-investigated the reaction between carbonyl chloride and ammonia, and found urea in the white solid product which he obtained.* He showed that if the gases were not thoroughly dried before being mixed, the amount of urea formed was so much diminished relatively to the amount of sal-ammoniac that it could not be recognised by adding nitric acid, which only throws down urea nitrate from a sufficiently concentrated solution of urea. Natanson describes his procedure as follows:—"I prepared the phosgene gas required for the investigation by leading carbon monoxide through boiling antimony perchloride. This method, recommended by Hofmann (*Ann.*, 1849, lxx., 139), I found very convenient. The two gases were led into a spacious dry glass balloon. The presence of urea in the white solid obtained could be shown, even by extracting it with absolute alcohol, evaporating the alcoholic extract to dryness, dissolving the residue in a little cold water, and adding strong nitric acid; urea nitrate separated at the latest in a few hours. All the urea formed can be obtained by adding a solution of baryta to the white solid product in sufficient excess to decompose the whole of the sal-ammoniac, evaporating the resulting liquid to dryness over sulphuric acid under the receiver of an air pump, and extracting the residue by absolute alcohol. The alcoholic extract having been evaporated to dryness and dissolved in a little water, sufficient ammonium carbonate must be added to precipitate any barium salt present. By adding strong nitric acid the urea can then be separated as its nitrate after sufficiently concentrating the filtrate. The treatment with ammonium carbonate cannot be omitted, because barium nitrate, which would be formed if the barium salts were not removed, is only very sparingly soluble in excess of nitric acid. The excess of ammonium carbonate used is mainly volatilised during the concentration, any small quantity which may remain in no way interferes with the reaction, as ammonium nitrate is very easily soluble in nitric acid." The precipitate thus obtained Natanson showed to be urea nitrate by analysis and by comparing its properties and behaviour with the salt otherwise prepared. He also isolated urea from it by decomposing it with potassium carbonate, and showed this to be identical with that obtained from urine.

Although the exact constitution of urea gave rise to some discussion at the time when opinions regarding molecular structure were settling down into their present form, the view now universally held, that urea is the amide of carbonic acid and of symmetrical structure, was established by Natanson's work, and no objection deserving of serious attention has ever been made to it. The arguments which have from time to time been brought forward in favour of an unsymmetrical structure have been based upon a want of sufficient recognition of the fact that a complex molecule is not a rigid structure, and that every part affects the affinities and relationships of every other part. The two NH_2 groups of urea ought not therefore to be expected to behave alike in all reactions, for since, in any given reaction, one must be first attacked, from this moment the properties of the other are modified, and consequently might not, indeed would not, behave exactly as the first had done.

Wöhler's synthesis could not be immediately employed for the preparation of substituted ureas, as at the time, and for more than twenty years afterward, the compound ammonias were unknown; indeed, it is interesting to recall that it was from the compound ureas that the first substituted ammonias were prepared by Wurtz.

Wurtz had synthesised methyl and ethyl cyanate, and tried, among other things, the action of a concentrated aqueous solution of ammonia upon them. By this treatment he obtained crystalline bodies which on investigation proved to be substituted ureas containing a methyl or an ethyl group in place of an atom of hydrogen. By heating these, which were solid substances easily isolated, with caustic potash, he obtained methylamine and ethylamine, another very notable discovery. In a note published fourteen years afterwards (*Repertoire de Chimie*

Pure, 1862, iv., 199), Wurtz definitely states:—"It was in studying the decomposition of these ureas that I discovered the compound ammonias."

Wurtz soon found that these and many similar primary amines could be formed directly by the action of potash on the cyanic esters.

Having obtained the amines, Wurtz at once substituted them for ammonia in the Wöhler synthesis,* and thus obtained a whole series of substituted ureas. He states the case very clearly (*Comptes Rendus*, 1851, xxxii., 414):—"The different terms of this series are formed, like urea itself, by the reciprocal action of the elements of cyanic acid and the elements of any ammoniacal base whatever. If, for example, one allows cyanic acid to react upon methylamine, there is formed a substance which stands in the same relation to ordinary urea that methylamine does to ammonia; that is, it is urea in which an equivalent of hydrogen has been replaced by an equivalent of methyl. It is methyl urea. To prepare it, it is sufficient to evaporate to dryness a solution of equivalent quantities of sulphate of methylamine and of potassium cyanate, and to take up the residue by alcohol. The cyanate of methylamine which is formed by double decomposition undergoes by the action of heat a metamorphosis analogous to that which ammonium cyanate undergoes. It becomes transformed into a true urea, which only differs from ordinary urea by the elements of CH_2 ."

Wurtz had found that the action of ammonia on the cyanic esters which gave rise to the first substituted ureas was a general reaction, and continues:—"Nothing would be more easy than to substitute for methylamine another ammonia, and to prepare by this method a series of bodies similar to urea in constitution and properties. It is more convenient, however, to obtain these bodies by another procedure which I indicated some years ago, and which consists in substituting for cyanic acid the cyanic ethers, and treating them directly with ammonia. Not only ordinary ammonia, but even the compound ammonias and certain soluble natural alkalis, react energetically with the cyanic ethers. The numerous compounds which one is thus able to obtain resemble urea closely in their more obvious characteristics; thus they are neutral to litmus; they combine more or less easily with nitric acid, and under the influence of potash they split up into carbonic acid and ammonia. . . . I call them compound ureas, because they are to be looked upon as ordinary urea in which one or more equivalents of hydrogen are replaced by one or more complex molecular groups."

In spite of various attempts, ammonium thiocyanate was not transformed into the sulphur analogue of urea until 1869, when Emerson Reynolds (*Trans. Chem. Soc.*, 1869, xxii., 2) showed that although, owing to the greater stability of ammonium thiocyanate, intramolecular rearrangement did not take place at 100°C ., it took place at temperatures above 180°C . With this synthesis of thiourea one important chapter in the history of the urea group was concluded. That much remains to be discovered, even regarding urea itself, is shown by the recent synthesis of its dichloro derivative.

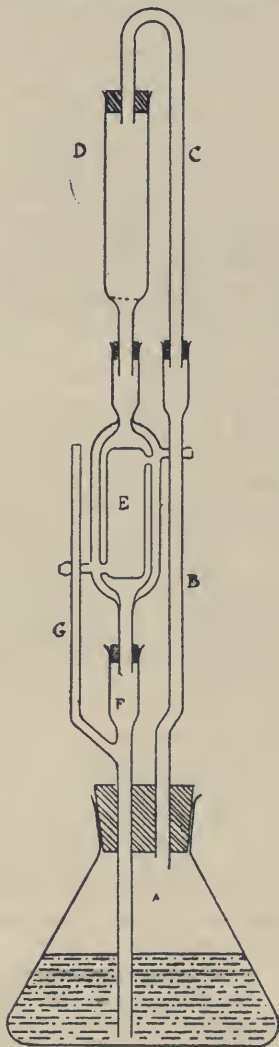
Substitution of Magnesium for Zinc in the Synthesis of Unsaturated Alcohols.—W. Jaworsky.—Magnesium can conveniently be used in place of zinc for the preparation of unsaturated alcohols by Saytzev's method under certain conditions. The reaction is performed in one phase, without previous preparation of the organo-metallic compound, and takes place in absolute ether. The mixture of allyl haloid and carbonyl compound must be added drop by drop at a rate regulated by the energy of the reaction, and the mixture may be dissolved in ether if the reaction is very rapid.—*Berichte*, xlii., No. 2.

* Hofmann had somewhat earlier (*Ann.*, 1845, liii., 57; and 1846, lvi., 265) prepared phenyl urea by the interaction of aniline sulphate and potassium cyanate,

A CONTINUOUS APPARATUS FOR EXTRACTING SOLIDS.

By NORMAN L. GEBHARD and F. BRYAN THOMPSON.

THE apparatus is arranged as in the figure. The extracting liquid is placed in the Erlenmeyer flask A, which is fitted with a two-holed cork. On boiling the liquid, hot vapours pass up the tube B, and hence into the wide tube D, which contains the substance to be extracted. The solid itself is kept in position in D by means of a small perforated porcelain disc held in the constricted part of the tube, and the



hot vapours in passing through D thoroughly extract the substance which it contains, and are then condensed in the double surfaced condenser E, and thence return to the flask. For safety purposes a small side arm, G, open to the air, is fused into the adapter F, and thus prevents the generation of pressure in the apparatus. If the positions of D and E are interchanged, the solid in D can then be extracted by percolation by the cold liquid condensed in E. The whole is very simple, and has been found extremely useful in many cases.

Chemical Laboratory,
The Technical College, Derby.

A SIMPLE NOTATION FOR INDICATING THE CONFIGURATION OF THE SUGARS AND ALLIED SUBSTANCES.

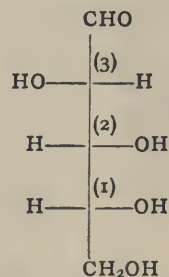
By T. S. PATTERSON.

IT is common knowledge that for the purpose of indicating the configuration of substances belonging to the sugar group, Emil Fischer has suggested the use of the signs + and - to represent the position of the -OH groups in a given molecule; thus, *d*-glucose = hexapentitol + - + +; *d*-saccharic acid = hexantetrolidic acid + - + + (or - - - + -); *d*-fructose = hexapentol-2-on - + +, &c. (E. Fischer, *Ber.*, 1894, xxvii., 3222); and that an attempt has been made by Lespieau (*Bull. Soc. Chim.*, 1895, [3], xiii., 105), and another by Maquenne ("Les Sucres et leur Principaux Dérivés," Paris, 1900), to introduce an even more comprehensive nomenclature. None of these methods, however, is of very great assistance to the memory. The two latter fail, perhaps, on account of their very comprehensiveness, and the first is not fully satisfactory, possibly because our minds are not trained to memorise a sequence of + and - signs. We have, however, become accustomed to register the positions of radicals by associating them with a sequence of letters or of figures, and in the following suggestion an attempt is made to translate, in as simple a way as possible, Emil Fischer's method into figures, somewhat after the manner of Lespieau and Maquenne. For this purpose the following conventions, which for the most part are already in use, are adopted.

1. The empirical names of the compounds under consideration are retained.* The present scheme makes no attempt, therefore, to indicate the chemical constitution of a given compound, and it thus remains necessary to remember, *e.g.*, that arabinose and lyxose are aldehydes with a chain of five carbon atoms; that erythulose, fructose, sorbose, tagatose are ketones; that dulcitol is entirely an alcohol; that mucic acid is a dibasic acid, and so on.

2. It is clear that it is only necessary to remember the configuration of one of any pair of antimeres. We may therefore fix our attention on the *d*-compounds.

3. Writing, *e.g.*, the formula for *d*-arabinose in Emil Fischer's manner, it is obviously only necessary to consider the distribution of the H- and -OH groups on one side of the formula. We may therefore select the right-hand side.

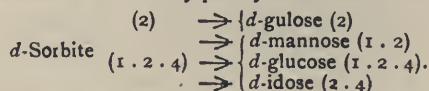


4. Since only two radicals, H- and -OH, come into consideration, we need only take account of one of these, and, following Emil Fischer, we choose the -OH groups.

5. If, then, the most highly oxidised end of the chain is always placed uppermost, the configuration of a compound may be accurately defined if we indicate by a symbol the

* The reason for so doing has been expressed by Emil Fischer (*Ber.*, 1907, xl., 103) as follows:—"Meine erwartung das diese rationellen Namen bald die alten empirischen Ausdrücke in den Hintergrund drängen würden, ist aber nicht eingetroffen. Im Gegenteil, für neu entdeckte Zucker mit geringerem Kohlenstoffgehalt sind seitdem immer noch empirische Namen gewählt worden, und ich ziehe daraus den Schluss, dass diese der Mehrzahl der Fachgenossen sympathischer sind, als die rationellen Ausdrücke, die man sich zum Verständnis immer erst in die Konfigurationsformel übersetzen muss."

- (a) *d*-Arabinose (1.2) by the cyanhydrine reaction must yield two compounds having the symbols (1.2) and (1.2.4). The former is *d*-mannose (1.2) and the latter *d*-glucose (1.2.4).
 (b) The connection between *d*-sorbitol and the hexoses derived from it is very plainly shown thus:—



- (c) The interconversion of the various members of the group can readily be followed (see II.).

The advantages of the system suggested above thus appear to be:—

1. The configurations of the compounds of the sugar group can be represented clearly by a simple numerical notation.
2. This allows of easy representation of the relationships and transformations of the compounds with *great saving of space*.
3. It is easily possible by very short study to memorise the numerical symbols, and, in consequence, the configurations of the substances in question.
4. The system is very useful for teaching purposes.

The University, Glasgow.

THE INFLUENCE OF MOISTURE ON CHEMICAL CHANGE.*

By Dr. H. BRERETON BAKER, M.A., F.R.S.

THE influence of a trace of water vapour on a chemical reaction was first noticed by Prof. H. B. Dixon in 1880. He found that it was possible to pass electric sparks in a mixture of carbon monoxide and oxygen without explosion, if the mixture had been very carefully dried. Shortly afterwards Cowper proved that dried chlorine had little or no action on several metals. Further observations were made by Prof. Dixon's pupils, the author in 1884 showing that carbon could be heated red-hot in dried oxygen, that sulphur and even the very inflammable phosphorus could be distilled in the same gas without burning. Later experiments proved that ammonia and hydrogen chloride gases could be mixed without uniting, and that the readily dissociated ammonium chloride could be converted into a true vapour, and that sulphur dioxide could be crystallised on lime, provided always that moisture was, as far as possible, removed. In 1902 it was shown that tubes containing very dry and pure hydrogen and oxygen could be heated to redness without any explosion resulting, and in 1907 that nitrogen trioxide could exist in the gaseous state if carefully dried.

Taken altogether, some twenty-five simple chemical actions have been shown to be dependent on the presence of moisture, and two only, the burning of cyanogen and carbon bisulphide, seem to take place as easily when dried as when moist. In 1893 Sir J. J. Thomson showed that a potential difference of 1200 volts was unable to cause the passage of electric sparks through very dry hydrogen, and in the same year the author was able to stop the passage of the discharge from an induction coil by carefully drying the gas between the platinum points.

The amount of water necessary for the bringing about of chemical action is extremely small, less in all probability than one part in three hundred thousand of the reacting gases. Many hypotheses have been suggested for the explanation of its action. Prof. Dixon believed in the case of carbon monoxide and oxygen, that the water vapour acted as a carrier of oxygen by alternate reduction and re-oxidation of the hydrogen. Traube imagined an alternate

formation and decomposition of hydrogen peroxide. Dr. Armstrong in 1884 suggested a theory of "reversed electrolysis," the impurity of the water vapour rendering it a conductor. Sir J. J. Thomson in 1893 published a paper showing that if the forces holding the atoms of a molecule together were electrical in their nature, these forces would be very much weakened in presence of liquid drops of any substance of high specific inductive capacity such as water.

In 1895 it was shown that the newly discovered Röntgen rays were able to cause a gas to become a conductor of electricity, and it was thought at that time that the molecules of the gas were split up into atoms by this agency. If this were so, it seemed likely that under these circumstances chemical action would take place in absence of water, but a joint paper of Prof. Dixon and the author, in 1896, showed that the Röntgen rays, at the ordinary temperature, had no measurable effect on the combination of dried gases. Since that time, however, the researches of J. J. Thomson, Rutherford, Townsend, and others have proved that the ionisation of gases is of a different character. The negative ions are extremely small particles of the mass of about 1/1000th part of the mass of an atom of hydrogen, the positive ion being the residue, but whether it is the residue of a molecule or of an atom seems to be still doubtful.

With the view of illustrating the influence of ionisation of gases on chemical change the author devised a new experiment. It is known that mercury vapour, under ordinary circumstances, contains only atoms of mercury which exhibit little tendency to combine with oxygen. The vapour, however, is ionised in the mercury vapour lamp, and when the current is cut off and oxygen is admitted shortly afterwards, the mercury becomes covered with a layer of mercuric oxide. Since the temperature of the lamp is much below that at which ordinary mercury vapour combines with oxygen, it is evident that in this case ionisation can bring about chemical action.

It is probable that this ionisation of mercury is different from the ordinary ionisation of gases. It may be regarded as the splitting off of an electron from the atom as distinct from a molecule, and the charged atom of mercury can then enter into union with oxygen. The two cases mentioned above of combustions in oxygen which are apparently unaffected by the absence of moisture, those of carbon bisulphide and cyanogen, are perhaps to be explained in the same way. Both gases are readily broken up into their elements, and it has been shown that carbon bisulphide breaks up at a lower temperature than that required for its burning. When these gases are heated, charged atoms are probably formed, capable of direct union with oxygen.

To test further the question as to whether the ionisation of molecules, as distinct from atoms, as in the case of mercury vapour, can bring about chemical change, some recent experiments were described in which radium bromide was used as the ionising agent. Small quantities of this salt contained in open silica tubes were sealed up in tubes containing mixtures of hydrogen and oxygen and carbon monoxide and oxygen, the gases being very dry in some cases and moist in others. In no case was any chemical action observed, although the tubes were allowed to stand at 20° for over two months. By means of a vacuum gauge the combination of 1/10,000 of the whole could have been detected. Another experiment showed that radium bromide was able to produce ionisation in very dry air, so that the want of chemical action in the above experiments must have been due to the fact that ionisation cannot of itself produce chemical action. There remained, however, the possibility of ionisation increasing the rate of union of two gases which were otherwise under conditions which would produce a slow chemical action between them. The reaction between nitrous oxide and hydrogen was found to be a suitable one for investigation, since it takes place slowly and uniformly at 530°. It is known that many substances when heated ionise gases. Lime is fairly effective

* Abstract of the Wilde Lecture, delivered before the Manchester Literary and Philosophical Society, March 9th, 1909.

In this respect, thoria to a much greater extent, and radium bromide is the most effective of all. Accordingly tubes containing the mixture of not very dry hydrogen and nitrous oxide were prepared. One contained a little lime, a second some thoria, and a third some radium bromide. These tubes were heated in an electric resistance furnace side by side with comparative tubes containing the same gases in which was a small quantity of powdered Jena glass to make the conditions as similar as possible. It was found that the rate of combination was much quickened by the presence of lime, much more by the presence of thoria, while the gases in contact with radium bromide, directly the combining temperature was reached, combined with explosion.

When a tube containing thoria and the same mixture was dried for ten days by phosphorus pentoxide, the gases showed no measurable combination when heated for five minutes to 530° . Hence increasing the ionisation in presence of moisture increases the rate of chemical change, while in absence of moisture it apparently has no effect.

An experiment of rather different type was shown which illustrates the way in which the ionisation of gases may exert its influence. A mixture of sulphur dioxide and sulphuretted hydrogen can be kept unchanged, although water vapour is present in some quantity. If, however, liquid water is introduced, separation of sulphur is immediate. A small open tube of radium bromide was placed in such a mixture, and after standing some time the whole of the gases condensed in the small tube of radium bromide in the form of sulphur and water. There is little doubt as to what happens in this case, the water vapour condenses in liquid drops on the ionised particles in the radium tube, and in these drops the reaction between the two gases is completed. In the other chemical changes at high temperatures it is conceivable that condensation to some form approaching the liquid state might take place, in which case Sir J. J. Thomson's theory would apply.

In support of this view must be mentioned some very recent experiments of Prof. J. S. Townsend, which show that a very great diminution in mobility of negative ions is produced when a mere trace of water vapour is added to a dried gas ionised by Röntgen rays. If there is any truth in this provisional working hypothesis, it should be found that ions and water vapour (or some similar substance) must both be present in a mixture of gases if action is to take place. Experiments already in progress seem to show that this is the case, but they have not been sufficiently often repeated for it to be desirable to publish the results at this stage.

The lecture was illustrated by experiments showing the influence of small quantities of moisture on chemical actions.

(NOTE.—The author finds that liquid water invariably collects in tubes containing salts of radium, though these salts are not at all deliquescent. In one experiment 10 mgrms. of radium bromide increased in weight by 1.5 mgrm. when allowed to stand for two days in an atmosphere saturated with moisture at 0° C.).

CHEMICALLY TREATED FLOURS.*

By E. F. LADD, Food Commissioner and Chemist.

(Continued from p. 112).

Pancreatic Digestion.—The next problem was to investigate the action of pancreatic digestion on the three different products. The pancreatic solution was prepared for this work according to the directions given by Simons, which are as follows:—

To 100 cc. of water 0.28 gm. of pancreatin and 1.15 gm. of NaHCO_3 were added. Two hundred cc. of this solution was used in each experiment.

Four experiments of pancreatic digestion were made, using in each case the raw gluten obtained from 10 grms. of flour. The following results were obtained:—

Pancreatic digestion of raw gluten from commercially bleached flour:—

No. of tube.	Time of digestion.	
	Hrs.	Mins.
1.	3	0
2.	3	30
3.	3	15
4.	3	0

The following results were obtained for the unbleached flour:—

No. of tube.	Time of digestion.	
	Hrs.	Mins.
1.	1	30
2.	2	0
3.	1	45
4.	2	0
5.	2	0

It will be noted that in the case of the bleached flour three hours or more were required for the complete digestion, while the unbleached digested in two hours or less.

Several tests of each case were made with baked gluten, but the difference, however, could not be so well established as the rate of digestion was so rapid that the difference in time was not as marked as with raw gluten.

Baked Gluten from Commercially Bleached Flour.

No. of tube.	Time of digestion.	
	Hrs.	Mins.
1.	0	45
2.	1	0
3.	0	45

Baked Gluten from Unbleached Flour.

No. of tube.	Time of digestion.	
	Hrs.	Mins.
1.	0	30
2.	0	45
3.	0	45

It will be noted that in every experiment in both cases the gluten digested in one hour or less.

The bread from bleached and unbleached flour was next tried with the following results:—

Bread from Bleached Flour.

No. of tube.	Time of digestion.	
	Hrs.	Mins.
1.	1	45
2.	1	45
3.	2	0
4.	2	0
5.	2	0

Bread from Unbleached Flour.

No. of tube.	Time of digestion.	
	Hrs.	Mins.
1.	1	15
2.	1	0
3.	1	0
4.	1	0
5.	1	30

By accident a much better test of digestion for the bread was discovered; that of digestion by means of the ordinary mould. Some of the bread used in the preceding experiments was allowed to stand in sealed Mason jars, and it was noticed that a large formation of mould appeared on the bread from unbleached flour in four days, while that from the commercially bleached flour remained free from any appreciable amount of mould for nearly ten days. However, the jars containing these samples of bread were not sterilised, and it was thought that this formation of mould might possibly be due to different conditions existing in the different jars. To determine this point the following experiments were carried out, in which we tried to make the conditions about the same.

* Special Bulletin from the Government Agricultural Experiment Station, Agricultural College, N.D., December, 1908.

Jars were sterilised in the hot-air oven at 115° C. and used in experiments which were carried out as follows:—

First Jar.—Bread made from unbleached flour was inoculated with some of the mould on the unbleached bread used in the above experiment.

Second Jar.—Bread made from bleached flour was introduced and inoculated with some of the same mould used in No. 1.

Third Jar.—Bread made from unbleached flour was introduced and inoculated with some of the mould on the bleached bread used in the former experiment.

Fourth Jar.—Bread made from bleached flour was introduced and inoculated with the same mould as in No. 3.

The reasons for making these two distinct tests in carrying out these experiments with the mould was due to the appearance of the mould on the bleached bread, as it seemed to be of a more destructive nature and it was thought that possibly it might be that it was of a different character. The results from the above experiments were as follows:—

The bread from the unbleached flour, in both cases, stood in the jars tightly sealed for two days before the mould made any appreciable show. The bread, however, from the commercially bleached flour, in both cases, resisted the action of the mould for five days.

The samples, however, were allowed to stand for ten days and further development noticed. The bread made from unbleached flour, at the end of this time, was almost entirely eaten up, while that from the bleached flour was well covered with the mould, but the texture remained good.

The tests with the mould indicate the same general conclusions as those brought out by the pepsin and pancreatic digestions, as it shows that the mould digests the bread with a marked difference.

The point might be raised that bleaching was a good thing as it acted as a preservative for the bread, but the pure food law wisely does not allow preservatives of other character, such as sulphites in meats, to be used, and this, no doubt, is similar in character so far as its effect is concerned.

The point was now brought up, if the nitric oxide acted upon the flour, what portions did it act upon—the starch, the gluten, or only on the fat? To determine this point the following observations were made:—

If the nitric oxide acted upon the starch it would, no doubt, form a very low nitrated nitro-starch product, and if this were the case, when treated with an acid, and heated up, would give off nitric oxide that would act upon starch, iodide paper, or a solution of starch and potassium iodide; but when 100 grms. of flour were treated in this manner, no such reaction was observed, showing, without doubt, that there could not be any action on the starch. However, it was noticed that a large amount of gas was given off, more than could be accounted for by being dissolved in the acid solution or by the expansion of the small amount of air left in the flask. This phenomenon was not noticed when unbleached flour was used.

The next problem now was to determine what this gas was, and as we had no action in the starch it remained either to be a decomposition product from fat or gluten.

A 50 grms. sample of bleached flour was then taken and the fat extracted. This fat was then treated in the same manner as the flour, but no such action was noticed; thus it could only be caused from an action on the gluten, but what this action was remained to be determined.

In studying over the reactions which might occur between such bodies as the protein bodies and nitric oxide, we will readily see the possibility of a diazo reaction, and if this occurred the gas should be nitrogen. A Schiff's azotometer was fixed up to collect such gas, and 100 grms. of flour was treated in the manner described above. After the complete apparatus had been filled with CO₂ to drive out all the air, then the acid, which had been previously boiled and was still warm, was introduced through a separating funnel, and the gases formed driven over into the

azotometer by more CO₂ (the CO₂ being absorbed by the KOH in the azotometer), the nitrogen collecting in the top over the KOH. A very small amount of the nitrogen was given off, but enough to be readily measured. This, however, if carried farther, would, no doubt, give means of determining the amount of NO₂ that actually went into the chemical combination; and, if the flour was over-bleached, the excess could then be approximately determined.

Further evidence to prove this point has recently been secured. In bleaching some flour to the limit to try to duplicate that which collects on the agitators and in other parts of the bleacher, it was also noticed that quite an appreciable heat was developed, indicating, no doubt, that a definite chemical reaction was going on. The flour also absorbed the first volume of nitric oxide with extreme readiness. Further, it was noticed that there was a point that this readiness of absorption by the flour was at an end, and in order to make the flour further take up more of the gas vigorous shaking was required, and the stream of gas had to be diminished.

This would seem to indicate that the gas acted on the gluten or some part of the gluten until its affinity for the gas was satisfied, and the further action was either a secondary action on the gluten or that a low nitrated nitro-starch was formed, which point is now under investigation.

The next work relating to this subject was done in the bleaching of different flours. A first patent durum flour was bleached with varying amounts of the nitric oxide under the same conditions, using 5 cc., 10 cc., &c., to the 100 grms. of flour. The one bleached with 20 cc., however, was slightly over-bleached. This blended with the best white hard wheat flour was used for a standard. The following mixture being made:—

Blended (per cent).	Standard (per cent).	Remarks.
10	90	} Could not be detected by slick.
20	80	
40	60	
30	70	

It is evident that by the ordinary tests that 30 per cent of durum could be introduced without detection. The same thing was tried with flour which was bleached, with 10 cc. NO₂ to 100 grms., with practically the same results.

Conclusions.

As the result of the experiments already given in the preceding pages, and in previous articles, we may summarise the facts in the following conclusions:—

I. That nitrous and nitric acid are two of the constituents formed from the bleaching of flour with nitrogen peroxide.

II. The nitrites and nitrates, or nitrite and nitrate reacting material, are among the products formed in the flour.

III. That bread as baked in the home by the domestic method will contain from one-third to one-half of the nitrite reacting material found in the flour.

IV. Oil properly extracted and purified from unbleached patent flour contains no nitrogen.

V. Oil extracted from bleached flour and purified by the same methods gives a strong reaction for nitrogen, thus confirming the statement made by Lewkowitsch.

VI. Oils from unbleached flours have an iodine absorption number (Hanus' method) of 101 or more, while the iodine absorption number for oils from bleached flours, when properly purified, will have a lower iodine number in proportion to the amount of bleaching.

VII. The difference in the iodine number and the difference in the nitrogen content of the oils show that the bleaching agent has acted upon the fat of the flour.

VIII. Flours aged for nine months showed no reduction in iodine number, while the same flour bleached and aged for the same length of time showed a reduction of 17-10 points, indicating that the artificial bleaching is not the same as the natural ageing of flours.

IX. The proportion of nitrates in the bread increases as the nitrates decrease.

X. The method of baking will determine to what extent the nitrates are changed or eliminated in the bread.

XI. Artificial digestion experiments with pepsin solutions show that the gluten from the unbleached flour was digested in four hours and fifty-seven minutes; while, under the same conditions, the gluten from the bleached flour was digested in eight hours and forty minutes.

XII. The baked gluten from the bleached and unbleached flours showed similar variations but not so wide, the time of digestion being much less; the same is true for the bread made from such flours.

XIII. In pancreatic digestion the glutens digested in 3·19 hours from bleached flour, and in 2·31 hours from unbleached flour. The time of digestion in pancreatic solutions of the baked gluten and of the bread was in favour of the unbleached product.

XIV. The experiments made with the keeping quality of bread made from bleached and unbleached flour demonstrated the antiseptic effect of the bleaching agent.

XV. It has been demonstrated that when the diazo or like action took place, the acid acted upon the gluten of the flour, changing its composition so that nitrogen gas was given off when the flour was treated with an acid.

XVI. The fact that the xanthoproteic reaction takes place demonstrates further that the bleaching agent has acted upon the gluten or the protein of the flour.

(To be continued).

PROCEEDINGS OF SOCIETIES.

THE INSTITUTE OF CHEMISTRY. *Annual General Meeting, March 1st, 1909.*

Professor PERCY F. FRANKLAND, the retiring President, in the Chair.

On the motion of Mr. A. GORDON SALAMON, Hon. Treasurer, seconded by Mr. ARTHUR C. CLAUDET, the Financial Statement for 1908 was received, and a vote of thanks accorded to the Hon. Auditors.

Mr. SALAMON said that, regarded as a business concern, the position of the Institute was sound for its present needs; it was paying its way and putting a little by, but it had not sufficient to meet the problem of the future, namely, the approaching expiry of the lease of its premises. During the year 1908, however, the improvement in the finances of the Institute had been more than fully maintained.

The PRESIDENT then submitted the Report of the Council, directing the attention of the Fellows and Associates to the principal items in the work of the Institute, to which he referred in more detail subsequently in his Address.

Dr. FRANK CLOWES, in seconding, said that he had attended many Annual Meetings, and it was a great pleasure to him to hear of the continued progress of the Institute in all its work and in new work. When he was a teacher, he always advised his students to work for the qualification of the Institute, and now that he was engaged as a professional chemist he was glad to see that the authorities of the London County Council fully recognised the value of A.I.C. and F.I.C.

The Report was received and adopted.

Prof. PERCY F. FRANKLAND, the retiring President, then delivered his Address. Whilst he regretted that the honour of representing the Institute had drawn to a close, it was by no means disagreeable to leave the responsibilities which the office of President involved. He was very thankful that through good fortune and the help of the Council and officers with whom he had been associated he was able to hand over the affairs of the Institute in as

sound and healthy a condition as when he took them over from his predecessor three years ago. The roll of the Institute had increased by seventy-eight Fellows, thirty Associates, and sixty-eight Students; and notwithstanding the increasing stringency of the regulations, the number of candidates for examination had increased from ninety-four (in 1906) to one hundred and fifty (1909). He believed these figures indicated that a real advance was taking place in the demand for highly trained chemists. He would emphasise the fact that whilst the well-being of the community was greatly promoted by the services of competent chemists, the mischief which could be wrought by the ill-trained and incompetent was incalculable. It was one of the chief duties of the Institute to maintain a high level of training for professional chemists by demanding of candidates for its membership evidence of thorough training, and by requiring them to pass searching examinations. Particular attention had lately been given to the educational side of the Institute's activity, and he referred to five important changes. Latin, hitherto compulsory, had been transferred to the list of optional subjects in the Preliminary Examination; the number of Examiners had been greatly increased, forming a Board the members of which were jointly responsible for the Examinations; written papers had been introduced in the Final Examinations; a working knowledge of French and German would shortly be required of all candidates for the Final Examination; and the Council now encouraged the holding of Examinations in India, in the Colonies, and in different centres of the United Kingdom. There was no finality either in the syllabus of the Examinations or in the courses of training demanded; such arrangements would require frequent remodelling in the future as the development of science and improvement of facilities of higher training might dictate and render possible.

The PRESIDENT then referred to the criticism of the Institute by Prof. Kipping in his Presidential Address to the Chemical Section of the British Association at the meeting last year, wherein he indicated that the Institute ignored the necessity of research work, and suggested that good research work should be insisted on in the case of all candidates for its Fellowship.

Professor FRANKLAND reminded the Fellows that the results of research were not necessarily recorded in the *Transactions* or *Proceedings* of the Royal Society, or in the pages of any scientific journal; those were mostly for academic researches. There was a vast amount of research involving originality and attainments of the highest order which from its very nature could not be published at all. Should chemists who are engaged on such research be debarred from the Fellowship because their names are not at the head of so many dozen pages apiece of the *Journal of the Chemical Society* or in a similar publication? He would assure Dr. Kipping that he had met chemists whose names are not associated with such academic researches who were nevertheless fully equipped and highly original investigators. Should these men not have been admitted to the Fellowship of the Institute? Succeeding Councils had built up an organisation of real flesh and blood, and not a paper Utopia. Could anybody deny that the Institute had by its policy during the thirty-two years of its existence enormously improved the theoretical and practical equipment of professional chemists in this country, and that it had stimulated hundreds to pursue courses of study which but for the Institute would never have been undertaken at all? Could it be denied that the examinations were specially distinguished as tests of original capacity as well as of theoretical attainments, manipulative skill, and knowledge of routine methods? Moreover, the Examiners were empowered to take into consideration any research work which any candidate might previously have carried out. He would yield to none in the advocacy of research as a part of training, but one must not be misled by an empty phrase or mere nomenclature. There was much training in originality of thought and experimental procedure which was not called research, and much of

what was called research that involved no originality in the thought or deed.

The President then referred to the work of the various Committees, indicating how the Institute had endeavoured to promote the interests of its members. He made special reference to protests made by the Council against professional chemists being invited to apply for appointments by tender, and appealed to the Fellows and Associates to assist in the endeavour to crush this sinister development. The Institute had lately taken steps to establish an Appointments Register, and had already succeeded in placing a number of members in good positions; steps would be taken to make manufacturers and other employers aware of the existence of this register, which promised to be most useful.

Passing to the most important item in his Address, the President intimated that a Special Committee had been discussing the arrangements to be made in view of the approaching expiry of the lease of the present premises of the Institute. The Committee had come to the conclusion that between ten and fifteen thousand pounds would have to be raised by voluntary contributions, in order to provide even a modest but dignified home in which the Institute could carry on its administrative work and conduct its examinations. They did not require a pretentious exterior or luxurious interior, but they wanted more commodious laboratories, offices, and library. The sum named left no margin for extravagance. The Committee had prepared a pamphlet setting forth the work of the Institute, discussing its present and prospective financial position, and giving a clear account of the aims in view, and the President urged the Fellows and Associates to read it carefully, after which they would, he felt sure, make such contributions as they could afford. Their joint action and personal sacrifice would continue to bear fruit in the time which is to come, long after they had become sleeping and forgotten members of that professional brotherhood in which it was their privilege now to be active workers.

After congratulating the Institute on the choice of Dr. GEORGE BEILBY, F.R.S., as the new President, Prof. FRANKLAND thanked the Fellows and Associates for their kindness and consideration during his term of office, remarking that such service as he had been able to give to the Institute had been rendered a labour so pleasant as hardly to partake of the nature of toil.

On behalf of the Fellows and Associates, the PRESIDENT then presented an Illuminated Address to Mr. DAVID HOWARD, in recognition of his services to the Institute in various capacities, as member of Council, Honorary Treasurer (eighteen years), President, Vice-President, and Censor, extending altogether over thirty years; at the same time congratulating him on the approach of his seventieth birthday, while yet retaining remarkably his health and vigour.

Mr. DAVID HOWARD, in reply, said that as a man grew old he began to think of what he had done. Whatever effort or labour he had devoted to the work of the Institute of Chemistry, he felt he did not deserve all the President had said. He had served on the Council under Sir Edward Frankland, and it was a great pleasure to receive the Address from his son. The founders of the Institute worked hard and with self-sacrifice for the Institute. They had nothing to gain, and were looked upon as wild enthusiasts in trying to make a profession of chemistry. There was at that time just a beginning of the profession; now the Institute could look back on the splendid work of the past, and it was for the younger men to work for its progress in the future.

On the motion of Mr. HOWARD, seconded by Prof. J. MILLAR THOMSON, a vote of thanks was accorded the President for his Address. Prof. Thomson endorsed much of what had been said on the subject of research.

The PRESIDENT having replied, the Report of the Scrutineers was received. The following were elected Censors:—Prof. Percy F. Frankland, Mr. David Howard, Sir William Ramsay, and Prof. J. Millar Thomson.

Mr. Walter F. Reid, Mr. G. T. Holloway, and Mr. R. E. Alison were elected Hon. Auditors, and the Officers and Council were declared elected as follows:—

President—G. T. Beilby, LL.D., F.R.S.

Vice-Presidents—B. Dyer, D.Sc.; M. O. Forster, D.Sc., F.R.S.; P. F. Frankland, LL.D., Ph.D., F.R.S.; O. Guttman, M.Inst.C.E.; E. G. Hooper; R. Meldola, F.R.S.

Hon. Treasurer—A. Gordon Salamon, A.R.S.M.

Members of Council—L. Archbutt; W. J. A. Butterfield, M.A.; R. F. Carpenter; F. H. Carr; C. E. Cassal, Col., V.D.; A. C. Chapman; F. D. Chattaway, M.A., D.Sc., F.R.S.; A. C. Claudet, A.R.S.M.; H. G. Colman, M.Sc., Ph.D.; J. H. Coste; A. W. Crossley, D.Sc., F.R.S.; W. W. Fisher, M.A.; W. C. Hancock, B.A.; O. Hehner; G. G. Henderson, M.A., D.Sc.; W. R. E. Hodgkinson, Ph.D.; F. G. Hopkins, M.A., M.B., D.Sc., F.R.S.; W. Macnab; G. McGowan, Ph.D.; G. T. Moody, D.Sc.; K. J. P. Orton, M.A., Ph.D.; W. J. Pope, M.A., M.Sc., F.R.S.; R. R. Tatlock; O. Trigger; J. A. Voelcker, M.A., B.Sc., Ph.D.; A. F. Watson, B.Sc.; W. M. G. Young.

With a vote of thanks to the retiring Officers and Members of Council, moved by Dr. EDWARD DIVERS, seconded by Mr. THOMAS TYRER, the meeting terminated.

SOCIETY OF CHEMICAL INDUSTRY. (LONDON SECTION).

Ordinary Meeting, March 1st, 1909.

Dr. LEWKOWITSCH in the Chair.

"On some Requirements of a Colour Standard." By J. W. LOVIBOND.

This paper deals with the various factors which influence the accuracy of observation in colour measurements and with some of the requirements of colour standards. It first treats of the advantages and disadvantages of some sources from which colour standards may be derived, such as the spectrum, pigments, light, &c. Then with the lights available for illuminating colours under examination, demonstrating the unreliability of direct lights, and showing how a reliable light may be obtained, demonstrating also the limits of luminous intensity between which colour measurements can be made. An important factor in the connection is the angle at which substances are viewed, it having been found that the different colours differ in this respect; red, for instance, varies greatly as the angle of incidence widens from forty degrees, whilst green is hardly affected. Other disturbing factors are dealt with, such as the differences in the colour intensity of pigments, the greater sensitiveness of trichromatic and printing and writing inks to light fluctuations compared to most other pigments.

"Studies on Malting. Part I. The Production of Diastase during the Germination of Barley on the Malting Floors." By ARTHUR R. LING, F.I.C., THEODORE RENDLE, and GEORGE McLAREN.

The authors discuss the present state of our knowledge on the production of diastase during the germination of barley, and conclude that this production is not restricted to that portion of the endosperm adjacent to the columnar epithelium of the scutellum as stated by Brown and Morris, but that it is formed in all parts of the endosperm. They have determined the diastatic power of sections of the corns of barley during several stages of the steeping and flooring processes, and have obtained the following results:—

During the steeping process the embryo is free from diastase, and the diastatic power of the barley remains constant. It is, however, possible that some augmentation of diastatic power occurs at this stage, for there is an apparent wandering of the enzyme towards the proximal

end of the corn. Since it is highly improbable that diastase diffuses, the probable explanation of this apparent wandering is that salts diffuse towards the embryo, leaving the diastase in the distal end less soluble and therefore less active, this being balanced by a small production of diastase in the other portions of the corn. On the floors there is a general increase in diastase in all parts of the corn, showing first in the proximal, then in the medial, and finally in the distal portion. The apparent production of diastase is greatly stimulated at the withering stage.

The authors' experiments prove that the bulk of the diastase, not only in the resting corn, but at all stages of germination, is localised in that portion of the endosperm adjacent to the columnar epithelium of the scutellum, which is in agreement with the observation of Brown and Morris. They consider that enzymes may be formed as katabolic products of protoplasm, and they reject as improbable the explanation of Brown and Morris that diastase is formed by the direct secretory powers of various organs. It seems probable, however, from the position in which enzymes occur in the corn, that they are preferably formed from reserve rather than from histological protein, although both are to be regarded as sources. The authors suggest that diastase may be formed by the action of the proteolytic enzyme on the protoplasmic contents of the cell, the process being one of autodigestion (Ford and Guthrie, *Journ. Inst. Brewing*, 1908, xiv., 61). They show that when barley flour is made into a dough with water, and kept at the temperature of the room, a considerable increase in diastatic power occurs.

"Sulphur as a cause of Corrosion in Steel." By G. NEVILL HUNTLY.

In a case of pitting in a stand-by boiler each pit was the centre of a blister. The liquid inside the blister was found to be quite different from the boiler fluid in composition, the former consisting of a slightly acid solution of ferrous sulphate, whilst the boiler water was alkaline with caustic soda. Reasons are given for supposing that the manganese sulphide in the steel is oxidised to sulphuric acid and an oxide of manganese, and that this acid acts locally on the surface of the boiler plate in the neighbourhood of the particle of manganese sulphide.

RÖNTGEN SOCIETY.

MR. ALAN A. CAMPBELL SWINTON read a paper on "*Some Vacuum Tube Phenomena*" at the last meeting of this Society on March 4th, and carried out a number of interesting experiments on high temperature effects with the cathode rays. One experiment of great interest was the entire conversion of a diamond into coke by means of the electric discharge. The cathode ray furnace for this purpose consisted of a glass tube with two concave cathodes focussing upon the diamond, which was placed upon an iridium plate supported by a platinum cup. Alternating current was applied to the terminals, and the temperature, measured by an optical pyrometer at the time of the diamond's conversion, was 1890° C. Mr. Swinton said that one of the points that could be investigated by this experiment was as to whether or not the diamond consisted of carbon containing dissolved in it one of the rare gases, such as krypton, argon, and neon. A spectrum of the residual gas was taken before the conversion of the diamond in the tube, and another spectrum after the conversion and the two spectra were practically identical. This seemed to prove conclusively the absence of these rare gases, although nitrogen and the commoner elements were found.

Speaking of the manufacture of rubies, Mr. Swinton said that in such an experiment it was very necessary to keep the current down relatively to the vacuum in order to avoid the "Canal" rays, which appeared suddenly and had a tendency to crack the glass. In the manufacture of rubies a little pellet of pure alumina was taken, and to this was added a small quantity of chromium. If chromium

were not used, sapphire was obtained instead of ruby. The ruby was mounted on a layer of alumina, which in the ordinary way fluoresced blue when bombarded by the cathode rays. After once being melted, however, it fluoresced red, but Mr. Swinton found that the red fluorescence was not due to the melting but to the presence of chromium, although the amount of chromium required to make the alumina fluoresce red was so small that if the alumina were put in a tube that had once been used for melting rubies there was always sufficient trace of chromium left in it to cause the red fluorescence.

A matter of particular interest to the Röntgen Society was also brought forward by Mr. Swinton. He had lately been making some experiments with regard to the blackening and consequent hardening of X-ray tubes. He made several pairs of cylindrical tubes, each pair having a kind of Siamese connection to a single stem. He made quite sure that the same amount of vacuum was in each tube, and then he allowed one of the tubes to become quite black upon its inner surface while its fellow remained quite clean. Under such conditions he found that it required twice as many volts to start the current through the black tube as through the clear one. His conclusion was that the mere presence of blackness on the inner surface of the tube increased its resistance, quite irrespectively of the degree of vacuum. In other words, the hardening and depreciated utility of the tube has nothing to do with the vacuum, but is due to the presence of a conducting film upon the glass.

A long discussion upon this effect took place, in the course of which Mr. W. DUDELL said that he thought it possible that the high resistance of the inner coating allowed the cathode to come nearer to the anode, thereby increasing the tube's resistance.

NOTICES OF BOOKS.

The Methods of Textile Chemistry. By FREDERIC DANNERTH, Ph.D. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1908.

THIS book gives exactly the course of practical work which is most suitable for the technical student who wishes to make a special study of the textile industries, and at the same time the chemist who is already engaged in such work will find that he can gather hints on practical methods from it. The first part deals with the qualitative analysis of wool and hair fibres, and describes methods of determining the physical differences between the various fibres, and thus identifying materials composed of or containing them. The reactions of the most important organic finishing materials are shown in a tabular form. Part II. discusses the quantitative analysis of various classes of fabrics, and also of the raw materials of which they are made, full experimental details being given for the performance of all the tests described. Methods of calculating results are explained by means of typical examples, and some tables of actual results obtained with various specimens of fibres are included. In the third part of the book a very short outline is given of a few important textile processes, such as cotton bleaching and mercerisation.

Les Erreurs de la Science. ("The Errors of Science"). By LOUIS-CHARLES-EMILE VIAL. Paris: Published by the Author. 1908.

THE author of this book believes that there are advantages to be gained by a return to the system of the ancients who believed in philosophising without appeal to experimental facts, and he advocates discarding modern methods of gaining knowledge by experiment, with a corresponding neglect of the exercise of the reason. Certainly, he cannot be accused of leaving hypotheses alone and searching for facts, and the book teems with the most fanciful flights of

the imagination. The fundamental argument, which is worked out at wearisome length, is that contraries are the generative principle of all acts, and that the Universe is nothing but a dynamical male and female couple of Force and Matter.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlii., No. 2, 1909.

Absorption of Hydrogen by Metallic Nickel.—A. Sieverts and Joh. Hagenacker.—According to the experiments of Sieverts and Beckmann, 1 volume of nickel between 377° and 580° absorbs 0.25 to 0.5 volumes of hydrogen, while Mayer and Altmayer have recently stated that much larger quantities of hydrogen are absorbed. The authors have performed many experiments with nickel at various temperatures, and have confirmed the former experimenters' results. They have also determined the influence of pressure on the absorption of hydrogen by nickel. At 822° and 923° the absorption is not proportional to the pressure, but is very nearly proportional to the square root of the pressure.

Triphenylmethyl.—M. Gomberg.—Triphenylcarbinol chlorides exist in a tautomeric condition in liquid sulphur dioxide, namely, as quino-carbonium salts. Their colour and also the mobility of the halogen atoms in the para-position must be ascribed directly to this tautomeric condition. As carbinol sulphates behave in all solvents like the carbinol haloids in liquid sulphur dioxide, it must be deduced that they are also quino-carbonium salts in all solvents. In a previous communication on triphenylmethyl, it was suggested from analogy that the acid carbinol sulphates, the double salts of the carbinol haloids with metallic haloids, and the metal-organic derivatives of the triphenylmethane series must all correspond to the quinoid type. Schmidlin has independently come to the same conclusion as regards the metal-organic compounds.

Some New Fluorides.—Otto Ruff.—Niobium pentafluoride, NbF₅, may be prepared by acting on niobium, obtained from the pentoxide, with elementary fluorine at 250°. It forms colourless, strongly refracting crystals which melt at 72° to 73°, and boil in glass vessels under 760 mm. pressure at 236°. The residue remaining in the flask is light blue. Niobium pentafluoride is very hygroscopic, quickly deliquesces in air, and gives a clear solution with water, without separation of niobic acid. With caustic soda fluoxyniobate is precipitated. Caustic soda and ammonia precipitate niobic acid from a solution of the fluoride in water. Tantalum pentafluoride, TaF₅, can be prepared by a similar method. It also forms colourless strongly refracting crystals which are hygroscopic and deliquesce in air. They melt at 94° and boil at 225° to 226.5°. Dry glass is attacked by tantalum pentafluoride only very slowly at the ordinary temperature, but at higher temperatures tantalic acid is formed. When uranium is subjected to the action of fluorine a violent reaction occurs, and a black mass is first formed, and then light green products, consisting chiefly of uranium tetrafluoride and containing some oxyfluoride, are obtained, while only small quantities of the hexafluoride can be prepared by this method. The reaction occurs far more quietly if uranium pentachloride is used instead of the metal itself. When heated with fluorine this readily yields the hexafluoride at a low temperature. UF₆ forms colourless monoclinic crystals, fuming in air. It sublimes on heating without melting. It is very hygroscopic, gives a clear yellowish green solution with water, and reacts with glass in presence of traces of water. The latter acts as a catalytic agent, and the products of the reaction are silicon tetrafluoride and uranium oxyfluoride.

Products of Arc and Spark Discharge in Liquid Argon and Nitrogen. Tin Nitride and Pyrophoric Tin.—Franz Fischer and George Iliovici.—The authors have studied the products of the arc and spark discharge of various metals in liquid argon and in nitrogen. When tin is used a substance is obtained which is a mixture of metal, nitride, and oxide. When this substance is heated pure nitrogen is given off. In subsequent experiments first the oxygen and then the nitrogen was removed from the liquid argon; oxides were first formed, then nitride, and finally pyrophoric tin. A gasometer was then constructed, in which the argon could be purified by means of a calcium arc. The calcium arc is not effective until the strength of the current is great enough to evaporate the calcium on the walls of the gasometer, and after such treatment the residue after ignition of the substance *in vacuo* is pure tin, and the generation of nitrogen gradually ceases altogether.

MISCELLANEOUS.

Royal Photographic Society of Great Britain.—An Exhibition of Photographs, by members of Societies affiliated with the Royal Photographic Society of Great Britain, at 66, Russell Square, will be open to the public daily (on production of visiting card) from March 10th to April 10th, between the hours of 11 a.m. and 5 p.m.; Saturdays, 11 a.m. till 2 p.m. A number of photographic societies throughout the kingdom (representing in all a membership of about 15,000) are affiliated to the Royal Photographic Society of Great Britain, and some of the best workers in these societies enter their pictures in an annual competition. These pictures are submitted to the Board of Judges, who select about fifty of the most noteworthy for circulation among the societies. The prints selected from the 1908 competition are now on view at the above address. These prints may be considered as representing the high-water mark in pictorial work attained by the members of the competing societies, and it is to the authors of these pictures that we look to maintain and raise the standard of photographic work in the future. A novel and educational feature in the present Exhibition is the inclusion of a number of sketches by W. J. Morgan, R.B.A., of Birmingham, who shows how a painter would treat the subjects selected by the photographers, and comparison of the pencil sketches with the photographic prints should be as interesting to the public generally as to those whose works have been selected for this distinction.

MEETINGS FOR THE WEEK.

TUESDAY, 16th.—Royal Institution, 3. "Evolution of the Brain as an Organ of Mind," by Prof. F. W. Mott, F.R.S.

WEDNESDAY, 17th.—Microscopical, 8. "Optical Examination of a Crystal Section in a Rock Slice," by Dr. J. W. Evans.

Royal Society of Arts, 8. "The Musical Aspect of Drums," by Gabriel G. Cleather (assisted by Mrs. Stanfield Prior at the Pianoforte).

THURSDAY, 18th.—Royal Institution, 3. "Recent Advances in Agricultural Science," by A. D. Hall, M.A.

Chemical, 8.30. "Iodine Dioxide," by M. M. P. Muir. "The Constituents of the Rhizome of *Apocynum androsaemifolium*," by C. W. Moore. "Action of Phosphorus Pentachloride on the Methylene Ethers of Catechol Derivatives—Part IV., Derivatives of Dihydroxyphenylacetic, glycolic, and glyoxylic Acids," by G. Barger and A. J. Ewins. "Studies in the Azine Series—Part I., The Constitution of Safranin," by J. T. Hewitt, S. H. Newman, and T. F. Winmill. "The Condensation of Amides with Esters of Acetylenic Acids," by S. Ruhemann. "Polarimetric Method of Identifying Chitin," by J. C. Irvine. "Studies in Asymmetric Synthesis—VII., Influence of the *d*-Amyl Group," by A. McKenzie and H. A. Müller.

FRIDAY, 19th.—Royal Institution, 9. "Experiments at High Temperatures and Pressures," by R. Threlfall, F.R.S.

SATURDAY, 20th.—Royal Institution, 3. "Properties of Matter," by Prof. Sir J. J. Thomson, F.R.S.

THE CHEMICAL NEWS.

Vol. XCIX., No. 2573.

THE METALLOIDS ARSENIC AND ANTIMONY FROM A THERMO-CHEMICAL STANDPOINT.

By J. C. THOMLINSON, B.Sc.

The hydrogen compounds of these elements, as well as those of nitrogen and phosphorus, show a continually decreasing heat of formation with increase of atomic weight.

	Heat of formation (cals.).
NH ₃	11·910
PH ₃	4·627
AsH ₃	-43·770
SbH ₃	-84·500

With the exception of ammonia, NH₃, these results are widely different from what we would be led to expect from a consideration of the heats of combination of phosphorus and hydrogen as derived from the chlorides of these elements (CHEMICAL NEWS, xcv., 145), and of those of the metalloids as derived from their respective chlorides. This is due to the fact that these hydrogen compounds are gases, and the elements phosphorus, arsenic, and antimony are solid at the temperature for which the data are reckoned, 18—20° C. Hence allowance must be made for the latent heats of fusion and volatilisation of these elements, and in general for the difference of heat content between the solid and gaseous state at this temperature.

If this correction were made, we would obtain a distinct proof of the correctness of the views which we are about to formulate as to the heats of combination of the metalloids, as well as to that of phosphorus, already dealt with.

The heats of formation of the trichlorides of these elements are given below, and we regard the atom of chlorine taking part in these reactions as having a heat value equal to 14·530 cals.

	Heat of formation (cals.).
PCl ₃	75·300
AsCl ₃	71·390
SbCl ₃	91·390

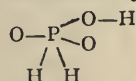
From these we at once find the heat of combination of trivalent phosphorus, arsenic, and antimony to be respectively 31·710, 27·800, and 47·800 cals.

Placed side by side with their atomic weights, the amounts of heat absorbed by phosphorus, arsenic, and antimony in assuming the gaseous state in their hydrides are seen to be roughly proportional to these atomic weights.

	Cals.	Atomic weight.
P	49·493	31
As	93·980	75
Sb	154·710	120

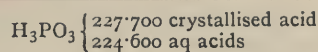
In this calculation, as in what follows, the heat of combination of hydrogen is taken to be 7·470 cals.

In dealing with the chlorides, oxides, and oxygen acids of these elements we will first take phosphorous acid,—



P≡	= 32·340
O=	= 71·405
	71·405
	52·545
	22·410

250·105

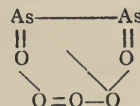


The result by experiment is comparable with that obtained by calculation.

Arsenic trichloride, AsCl₃ has a heat of formation 71·390 cals., giving us trivalent arsenic, As≡ = 27·800 cals. :—



If we regard arsenic trioxide as having the above structural formula, with trivalent oxygen O≡ = 33·685 cals., the calculated heat of formation is 156·655 cals., the experimental value being 154·670 cals.



Similarly, with arsenic pentoxide and one valency of an oxygen atom exerting a central influence in the molecule, the calculated and experimental heats of formation are 224·025 and 219·330 cals. respectively.

As regards antimony, I have no data at hand for the anhydrous oxides.

A SIMPLE METHOD FOR DETERMINING VAPOUR-DENSITIES.

By PHILIP BLACKMAN.

AMONG the references at the beginning of the paper in the CHEMICAL NEWS, 1909, xcix., p. 87, should be included *Zeitschrift für Physikalische Chemie*, 1909, lxx., 550 (but read there *l* instead of *S* and *l_c* instead of *S_c*). Also, in the CHEMICAL NEWS (*ibid.*), instead of—

$$d = \frac{31068 w l L_c (273 + t_1)}{\rho L (V + h) (L_c - L)}$$

read—

$$d = \frac{31068 w l L_c (273 + t_1)}{\rho L (V + h) (L_c - l)}$$

CHEMICALLY TREATED FLOURS.*

By E. F. LADD, Food Commissioner and Chemist.

(Concluded from p. 129).

II. EFFECT OF BLEACHED FLOUR EXTRACTS ON RABBITS.

By E. F. LADD and H. L. WHITE.

AFTER reading the Address of Prof. Shepard, of South Dakota, with regard to the effect of nitrous acid in retarding or inhibiting digestion, and after considering the effect of other food preservatives, as reported upon by Dr. Wiley in various reports of experiments carried on by the Bureau of Chemistry, Department of Agriculture, it has seemed that, if flours contained varying quantities of nitrous acid, nitrites, or other toxic bodies, extracts from such flours would, if fed to animals, result in some physiological action, and especially in action upon the blood corpuscles, diminishing the oxyhemoglobin with a corresponding increase in the methemoglobin, and in showing other conditions which would be noticeable when the various parts

* Special Bulletin from the Government Agricultural Experiment Station, Agricultural College, N.D., December, 1908.

and organs of the body were carefully examined. It was then, after consultation with Dr. Van Es, decided to undertake such an experiment. A large amount of preliminary work in methods of extraction and the preparation of samples was undertaken in order to find out how best to prepare extracts which could be used.

The first attempt was to prepare an aqueous extract of three samples of flour—the unbleached, the commercially bleached, and the over-bleached, the latter being for the purpose of magnifying the results. It was found, in the case of the commercially bleached flours, impossible to concentrate the aqueous extracts without losing in the distillate of water all of the nitrous acid or nitrite reacting material, and this part of the experiment was, for the time being, necessarily abandoned until a method could be devised whereby concentration could be secured under such conditions as to permit of retaining the toxic material which might be extracted.

These experiments were carried on with the assistance of Prof. White and Dr. Van Es. The results of these experiments are indicated in the following detailed report:—

In order to determine the effects of bleached flour on an animal organism, alcoholic extracts of over-bleached and commercially bleached flours were prepared and administered to rabbits. As a control alcoholic extracts of an unbleached flour were also prepared and administered to rabbits; and, as a further check, physiological salt solutions containing alcohol, ranging from 7 to 16 per cent, were administered to other lots of rabbits.

The flour having the laboratory number 5489 was found to be commercially bleached, the same having been purchased on the market, and was used to prepare the alcoholic residues. This flour contained 3.0 parts per million of nitrite reacting nitrogen, or as sodium nitrite 15.0 parts. The flour No. 204 was used for the unbleached residues. Some of this same flour (No. 204) was subjected to the action of nitrogen peroxide until it assumed a marked yellow colour, and this product was used in the preparation of the over-bleached residues. The nitrogen peroxide used in this bleaching was generated by allowing nitric acid to act on strips of copper. The gas as generated was passed through a 20-inch coiled reflux condenser in order to condense all free acid, and the gas so collected was used in the preparation of the over-bleached flour.

The alcoholic extracts were prepared by shaking up portions of 2000 grms. of the flour, in lots of 500 grms. each, with 95 per cent alcohol. The shaking was continued at intervals for several days. The alcohol was then distilled off in an atmosphere of hydrogen and under reduced pressure. The residue in each case was a little less than 100 cc. The residue from the over-bleached flour was so thick and viscous that it was found necessary to add a little alcohol so that it could be made thin enough to be administered. About 7 cc. of alcohol was added to the residue from the over-bleached, and that from the commercially bleached flours, enough to bring the volume of each residue up to 100 cc.

The residue from the alcoholic extracts of over-bleached flour was, as already stated, a thick viscous substance, orange-yellow in colour, strongly acid in reaction, and having a strong odour. When put on the hands it made a yellow stain which was removed with considerable difficulty. When a small portion of the residue was moistened with ammonium hydroxide it gave a reaction similar to the xanthoproteic reaction, which is obtained by boiling proteid material with nitric acid, cooling, and then moistening with ammonium hydroxide.

The alcoholic residues from the commercially bleached and from the unbleached flours were thin yellow liquids, slightly acid in reaction. The alcoholic extracts were administered to rabbits by means of a stomach tube and a syringe, and in each case, before withdrawal of the tube, it was rinsed out with distilled water. By the use of the stomach tube none of the acid residues came in contact with the esophagus, so that the possibility of death from a secondary cause, such as strangulation, was eliminated.

RESULTS OF EXPERIMENTS.

Series II.

Alcoholic Extract, Over-bleached Flour. Amount of extract 100 cc. Each rabbit marked with string in ear.

Rabbit No.	Amount (cc.).	Remarks.
1 (large grey)	15	Collapse in fifty minutes; died in three hours.
2	10—12	Violent convulsions; dead in fifteen minutes.
3	10—12	Collapse in fifty minutes; dead in three hours.

Post-mortem Findings by Dr. L. Van Es.—All examinations were made immediately after death to exclude, as far as possible, post-mortem changes.

Series II.: Rabbit No. 1.—Heart in diastole; lungs slightly hyperemic; liver blenched; where it has been in contact with the stomach, the liver has a boxwood colour; kidneys salmon coloured, and cut surface is pinkish in colour; stomach walls come asunder when slightly pulled; on section, there is noticed complete erosion of mucosa which strips off easily, blood not coagulated.

Rabbit No. 2.—Lungs not contracted by hyperemic, emphysematous, liver hyperemic, blenched wherever in contact with stomach walls, stomach contents escaped owing to almost complete erosion of stomach walls, kidneys slightly hyperemic, blood not coagulated.

Rabbit No. 3.—Lungs fully contracted, blenched on surface with hyperemic areas, heart in diastole, liver hyperemic, and where in contact with stomach walls, blenched and friable, stomach walls almost completely eroded, blood not coagulated.

Series IV.

Alcoholic Extract, Commercially Bleached Flour. (Flour No. 5489). Amount of extract 100 cc. Rabbits marked with string in ear. Pen V. (Sept. 16, 1908, 11.30 a.m.).

Rabbit No.	Amount (cc.).	Remarks.
1	10	Collapse in thirty minutes; dead in three and a-half hours.
2	10	Collapse in thirty minutes; dead in three and a-half hours.
3	10	Collapse in forty minutes; recovered and seemed well at 8 a.m., Sept. 17.

Extract had a decided odour of alcohol; contained about 7 per cent.

Second Administration (Sept 17, 1901, 11 a.m.).

Rabbit No.	Amount (cc.).	Remarks.
3	10	Immediate collapse and dead in fifteen minutes.

Series IV. Post-mortem Findings: Rabbit No. 1.—Lungs normal, heart in diastole, blood poorly clotted, liver, somewhat congested, kidneys normal, intestines normal, spleen normal, stomach intact, contents slightly acid, hyperemic condition with erosion of mucosa, walls somewhat edematous; stomach preserved in 4 per cent formalin.

Rabbit No. 2.—Heart in diastole, lungs hyperemic, blood poorly clotted, kidneys normal, intestines normal, spleen normal, liver hyperemic, stomach intact, contents acid, wall of stomach edematous with slight superficial erosion of mucosa. Stomach preserved in 4 per cent formalin.

Rabbit No. 3.—Lungs normal, heart in diastole, blood clotted normally, intestines normal, kidneys slightly congested, liver normal except slightly blenched where in contact with stomach, spleen normal, stomach intact, contents acid, stomach shows slight superficial erosion, no hyperemia.

Alcoholic Extract of Unbleached Flour. Amount of Extract 100 cc., Pen II. (Sept. 16, 1908, 11.45 a.m.).

Rabbit No.	Amount (cc.).	Remarks.
1	10	Some discomfort manifested for
2	10	two or three hours, but seemed
3 (large grey)	15	all right again in five hours.

Second Administration (Sept. 17, 1908, 11.15 a.m.).

1	10	Did not seem to affect rabbits in
2	10	any way.
3	15	

Third Administration (Sept. 18, 1908, 11 a.m.).

1	10	Did not seem to leave any effect.
2	—	
3	15	

Series VII.

Physiological Salt Solution. Pen II. (Sept. 16, 1908, 12 noon).

Rabbit No.	Amount (cc.).	Remarks.
1	10	Rabbits not affected.
2	15	
3	10	

Second Administration (Sept. 17, 1908, 11.30 a.m.).

1	10	Not affected.
2	12	
3	15	

Third Administration (Sept. 18, 1908, 11.15 a.m.).

1	10	Not affected.
2	15	
3	15	

Series VIII.

Physiological Salt Solution containing Alcohol. Pen III. (Sept. 16, 1908, 12 noon).

Rabbit No.	Amount (cc.).	Remarks.
1	10	Salt solution contains 7 per cent
2	10	alcohol. Not affected.
3	12	

Second Administration (Sept. 17, 1908, 11.30 a.m.).

1	10	Salt solution contains 14 per cent
2	15	alcohol. Not affected.
3	15	

Third Administration (Sept. 18, 1908, 11.15 a.m.).

1	10	Salt solution contains 16 per cent
2	10	alcohol. Not affected.
3	12	

The results of these experiments were so striking that when taken together with previous investigations made by the department would seem to indicate that other toxic bodies, aside from nitrites, must be present in the flour, and this bears out the results of tests previously made on the fat as indicating a nitrated or nitro derivative resulting from the action of bleaching agents upon the fat or oil of the flour; and, further, indicates the correctness of the assumption based upon the experiments that nitrous acid or nitric acid, or products resulting therefrom, have reacted upon the gluten, apparently producing, as previously shown, diazo compounds, and it is a well known fact that some of the diazo compounds are exceedingly poisonous. If this is true then there should be remaining in the aqueous extract, from the over-bleached flour, sufficient of other toxic bodies to produce some physiological effect when fed to rabbits, although all of the nitrous acid or nitric reacting material was lost in the distillate in the attempt at concentration.

However, the aqueous extract or residue prepared from over-bleached flour, the same as was used for preparing the alcohol residue from over-bleached flour, was tested.

The aqueous extract was brown or blackish in colour, of syrupy consistency, had the odour of caramel, and gave a strong acid reaction. 200 cc. of this extract was prepared of such a strength that 10 cc. represented the extract from 100 grms. of flour, or, approximately, the amount of extract from the flour which would be used in the preparation of one-fourth loaf of bread.

The results of feeding experiments as conducted in previous cases were as follows:—

Series I.

Aqueous Extract of Over-bleached Flour. Amount of Extract 200 cc. Pen I. (Sept. 16, 1908).

Rabbit No.	Amount (cc.).	Remarks.
1 (large grey)	15	Collapse in ten minutes; dead in two to two and a-half hours.
2	10	Collapse in ten minutes; dead in twenty to thirty minutes.
3	10	Collapse in ten minutes; dead in twenty to thirty minutes.

Series I.: Rabbit No. 1.—Stomach contents show strongly acid, and have escaped into peritoneal cavity owing to perforation of stomach by erosion. Where stomach contents have been in contact with the liver, the liver tissue is friable and blenched on the surface. Escape of stomach contents is probably post-mortem owing to lack of inflammatory changes. Heart in diastole, lungs hyperemic, kidneys slightly hyperemic, blood poorly coagulated.

Rabbit No. 2.—Stomach yet intact, but on withdrawal, stomach walls pull asunder. On inner side evidence of hyperemia of mucosa. Liver friable and blenched on surface, kidneys hyperemic, lungs hyperemic, heart in diastole, intestines apparently normal, blood poorly coagulated.

Rabbit No. 3.—Lungs hyperemic, heart in diastole, blood poorly coagulated, liver hyperemic, kidneys slightly hyperemic, stomach intact, mucosa eroded and adhering to stomach contents.

In a previous series of experiments alcoholic and aqueous solution of over-bleached flour were fed to rabbits with fatal results, death resulting in from fifteen minutes to three hours. At the post-mortem examinations of these rabbits it was found that the stomach of each rabbit was either perforated or easily pulled apart, indicating that the extracts exerted on the stomach walls a marked corrosive action. As these extracts had a strong acid reaction, and in order to determine whether the extracts had a toxic as well as corrosive effect, both extracts were neutralised with sodium bicarbonate, and then administered as in the previous series of experiments.

Series IX.

Aqueous Extract Over-bleached Flour, neutralised with sodium bicarbonate. Pen IV. (Oct. 12, 1908, 4.40 p.m.).

Rabbit No.	Amount (cc.).	Remarks.
1 (grey)	12	Hindquarters paralysed in one hour. Died during night of Oct. 12th.
2 (white and grey)	12	Prostrate in ten minutes—heavy respiration—convulsions, died in one hour.

Series X.

Alcoholic Extracts Over-bleached Flour, neutralised with sodium bicarbonate. Pen II. (Oct. 12, 1908, 4.30 p.m.).

Rabbit No.	Amount (cc.).	Remarks.
1 (grey)	12	After ten minutes would not eat; stretched out on floor.
2 (white)	10	

Second Administration (Oct. 14, 1908, 4.30 p.m.).

1	8	Survived treatment, but was not in
2	8	good condition. Died during night.

Post-mortem Findings. Series IX: Rabbit No. 2.—No coccidiosis in liver, heart normal, stomach congested, lungs normal, kidneys congested, odour of viscera same as that of extract, mucosa of stomach congested.

Rabbit No. 1.—Same findings as for rabbit No. 2.

Series X: Rabbit No. 2.—Stomach congested, liver showed coccidiosis.

Alcoholic Extract of Unbleached Flour.

A second alcoholic extract of unbleached flour was prepared by extracting 2000 grms. of flour with alcohol and concentrating to 100 cc. over a low flame. The extract was a thick liquid with the odour of alcohol, and on standing separated into two layers. The top layer was brown in colour, and looked like a fat; the lower layer was straw-coloured. This extract was administered to rabbits in the manner as in previous experiments.

Series. XI. (Oct. 20, 1908, 5 p.m.).

Rabbit No.	Amount (c.c.).	Remarks.
1	15	No ill effects noted.
2	15	
3	12	

Second Administration (Oct. 21, 1908, 4 p.m.).

1	15	No ill effects noted.
2	15	
3	—	

The fact seems to have been clearly established that commercially bleached flour, such as we found on the market and purchased for use in this experiment, did contain toxic bodies in sufficient quantity to cause death in animals to which the same was fed as an extract.

Conclusions.

As the result of the experiments presented in this and other reports we feel justified in summarising the following facts:—

I. There is produced in flour, as the results of artificial bleaching, toxic bodies.

II. Experiments previously reported indicate the possibility of a diazo reaction where flour has been subjected to bleaching, especially when the bleaching has been carried to a considerable extent.

III. The fact that the xanthoproteic reaction takes place demonstrates that the bleaching agent has acted upon the gluten or the protein of the flour.

IV. Alcoholic extracts prepared from unbleached flour and fed to rabbits did not affect them.

V. Alcoholic extracts prepared in the same manner from commercially bleached flour and fed to the rabbits in the same way caused their death within a few hours.

VI. Alcoholic extracts prepared from over-bleached flour in the same manner and fed in the same way to rabbits caused their immediate collapse and death.

VII. Aqueous extracts prepared from over-bleached flours when fed to rabbits caused their immediate collapse and death.

VIII. Alcohol and aqueous extracts from over-bleached flour, when neutralised with sodium bicarbonate, and fed to rabbits, caused the death of the rabbits in a short time, demonstrating that it was not the acidity that produced the death of the rabbits.

IX.—In preparing aqueous extracts all nitrite reacting material disappeared; hence, the death of the rabbits; in this case, must have been due to the presence of other toxic material than that of nitrites.

While no decision has been rendered, at the time of this writing, by the District Court, it is of interest to the public to know that the Secretary of Agriculture, after carefully considering the question of bleached flour in all its phases, has recently rendered a decision with regard to the status of flour bleached by chemical means under the Food and Drugs Act of June 30th, 1906. This decision is fully set forth in the following telegram:—

Washington, D.C., Dec. 9th, 1908.

“E. F. LADD, Fargo, N.D.

“You are advised that I have to-day issued the following decision relative to bleached flour:—

Bleached Flour.

“Flour bleached with nitrogen peroxide, as affected by the Food and Drugs Act of June 30th, 1906, has been made the subject of a careful investigation extending over several months. A public hearing on this subject was held by the Secretary of Agriculture and the Board of Food and Drug Inspection, beginning November 18th, 1908, and continuing five days. At this hearing those who favoured the bleaching process and those who opposed it were given equal opportunities to be heard. It is my opinion, based upon all the testimony given at the hearing, upon the reports of those who have investigated the subject, upon the literature, and upon the unanimous opinion of the Board of Food and Drug Inspection, that flour bleached by nitrogen peroxide is an adulterated product under the Food and Drugs Act of June 30th, 1906. That the character of the adulteration is such that no statement upon the label will bring bleached flour within the law, and that such flour cannot be legally made or sold in the District of Columbia, or in the territories, or to be transported or sold in interstate commerce, or be transported or sold in foreign commerce except under that portion of Section 2 of the law which reads:—

“Provided, that no article shall be deemed misbranded or adulterated within the provisions of this Act when intended for export to any foreign country, and prepared or packed according to the specifications or directions of the foreign purchaser, when no substance is used in the preparation or packing thereof in conflict with the Laws of the foreign country to which said article is intended to be shipped.

“In view of the extent of the bleaching process, and of the immense quantity of bleached flour now on hand or in process of manufacture, no prosecutions will be recommended by this Department for manufacture and sale thereof in the District of Columbia or the territories, or for transportation or sale in interstate or foreign commerce for a period of six months from the date hereof.”

(Signed) JAMES WILSON, Secretary of Agriculture.

IMPROVEMENTS IN PRODUCTION AND APPLICATION OF GUNCOTTON AND NITROGLYCERIN.*

By Colonel Sir FREDERIC L. NATHAN, R.A.

THE subject on which I have been asked to lecture to-night is one that has often been dealt with in this theatre by such great authorities as the late Sir Frederick Abel and Sir Andrew Noble. I feel it a great honour, therefore, to have been invited to deliver this discourse, but I realise that it is a very difficult task I am attempting. Sir Frederick Abel was one of the greatest authorities on the chemistry of explosives, and used to deal with them mainly from the chemical point of view; Sir Andrew Noble, on the other hand, is the greatest living authority on all that concerns artillery and ballistics, and he has considered explosives mainly from the ballistic standpoint. I am neither a chemist nor an artilleryman, but occupy the much more humble position of a manufacturer of explosives, and I must ask your indulgence whilst I endeavour to describe the main features connected with the manufacture of guncotton and nitroglycerin, and to say a few words about cordite, essentially a combination of the two.

For centuries the only explosive known to the world was that mechanical mixture of saltpetre, charcoal, and sulphur, called gunpowder. Chemical explosives may be said to

* A Discourse delivered before the Royal Institution, January 29, 1909.

date from the discovery of guncotton by Schönbein, and it is a fact worth noting on this occasion, that the first sample of guncotton in this country was one which accompanied a letter of Schönbein from Basle, dated March 18th, 1846, and addressed to Michael Faraday at the Royal Institution. Schönbein referred to guncotton in this letter as follows:—

"There is another point about which I take the liberty to ask your kind advice. I am enabled to prepare in any quantity a matter which, next to gunpowder, must be regarded as the most combustible substance known. So inflammable is that matter that on being brought in contact with the slightest spark, it will instantly be set on fire, leaving hardly any trace of ashes, and if the combustion be caused within closed vessels, a violent explosion takes place. That combustible substance is, as I will confidently tell you, raw cotton, prepared in a simple manner, which I shall describe you hereafter. I must not omit to mention that water has not the least action upon my matter; that is; that it may be immersed ever so long in that fluid without losing its inflammability after having been dried again. A substance of that description seems to be applicable to many purposes of daily life, and I should think that it might advantageously be used as a powerful means of defence and attack. Indeed, the Congrevean rockets can hardly be more combustible than my prepared cotton is. What shall I do with that matter? Shall I offer it to your Government? I have enclosed a little bit of that really frightful body, and you may easily convince yourself of the correctness of my statements regarding its properties."

In a subsequent letter he gave this body the name of guncotton.

Attempts to manufacture guncotton in accordance with the method devised by Schönbein were made both in this country and abroad. Accidents which occur, however, both in great Britain and France in the early days of manufacture, led to the abandonment of attempts to produce it in these countries; it was only in Austria that its production was persevered with, and a system of manufacture worked out there by Baron von Lenk. Having succeeded in producing guncotton on the manufacturing scale, von Lenk turned his attention to adapting it for propulsive purposes, and although at one time his efforts appeared to have met with a certain amount of success, and batteries of field artillery in Austria were actually equipped with guncotton cartridges, the difficulty of moderating its rate of combustion was never satisfactorily overcome. While this question was still the subject of experiments, serious accidents, due to the spontaneous combustion of guncotton in store, led to its production being given up even in Austria.

In 1863, Sir Frederick Abel took up the study of the manufacture of guncotton in this country with a view to adapting it for propulsive purposes, and, at the same time, to improving its stability, so that its spontaneous combustion in store might be prevented.

He was not successful in the first object, but as regards the production of guncotton of good stability, the modifications that he introduced into the von Lenk system of manufacture resulted in the production of stable guncotton.

The process of manufacture devised by von Lenk was briefly as follows:—

Skeins of long staple cotton yarn were immersed in a mixture of strong nitric acid of 1.52 sp. gr., one part, and sulphuric acid of 1.84 sp. gr. three parts, contained in iron pans. The skeins were stirred about in the acid bath for a few minutes, removed to a grating above it, and some of the acid squeezed out with a suitable iron tool. The cotton, while still thoroughly wetted with acid, was transferred to earthenware pots, in which it remained for forty-eight hours. The pots stood in cold water to prevent decomposition of their contents. At the end of two days the conversion of the cotton into guncotton was complete; the skeins were removed from the pots, and as much as possible of the acid removed in centrifugal wringing

machines. After centrifuging, the skeins were drowned as rapidly as possible in a cascade of water, the object being to remove the rest of the free acid. The final purification was effected by immersing the skeins for about three weeks in running water, boiling for a few minutes in an alkaline solution, and finally washing for a few days in flowing water.

In all that concerned the actual process of nitration, Abel followed von Lenk, but instead of using skeins of long staple cotton, he introduced the use of cotton waste from the spinning mills, suitably cleaned; and after the free acid had been removed in the preliminary drowning, the guncotton, still in the same physical condition as the cotton waste from which it had been produced, was reduced to a fine state of division in a beating-engine. The effect of this important modification was to remove the last traces of "free acid" and of unstable bodies, so that the prolonged washing in cold water could be dispensed with, and at the same time, a much more stable product be obtained.

Cotton fibre is of a tubular structure, and as long as these tubes exist in long lengths, the impurities in the interior of the tubes, derived from the evaporated juices of the cotton plant, and more or less affected by the nitration process, are extremely difficult of removal. Not only is the cotton in the form of long tubular fibres, but these fibres are themselves matted and entwined to such an extent that the former process of washing in running water even failed to remove impurities from amongst the bundles of fibre.

The operation of pulping introduced by Abel breaks up both the bundles of fibre and the fibres themselves, reducing the latter to short lengths or destroying them altogether by crushing. In this fine state of division the removal of impurities is much more readily effected by washing.

The manufacture of guncotton by the von Lenk-Abel process was commenced in this country about 1865. Foreign countries took it up in quick succession, and the process was the one universally followed for the next forty years. Some modifications of the nitration process were made towards the end of that period, in one case in the direction of dipping larger charges of cotton waste, and of allowing them to remain in the original acid mixture until nitration was completed, and then transferring the whole contents of the nitrating pan into the acid centrifugal; in another case the nitration process was actually carried out in the centrifugal itself.

In 1905, however, an entirely new system of nitration, hereafter referred to as the "displacement process," was invented by Messrs. Thomson, of the Royal Gunpowder Factory, and this process has been perfected and has entirely replaced the pot system of nitration there, and at Nobel's Explosives Factory at Ardeer, in Scotland. It is also being adopted at other factories both in this country and abroad.

The nitration of the cotton waste is carried out in shallow circular earthenware pans. These pans are grouped together, and worked in sets of four. The bottom of the pan slopes downwards to a central hole, connected by suitable pipes and cocks to a pipe supplying the nitrating acid, and to other pipes to which the waste acid is removed on completion of nitration. The pans are covered with aluminium hoods connected to an exhaust-pan, for carrying off fumes.

Nitrating acid is then run in up to a definite mark, and a charge of 20 lb. of dry cotton waste is immersed in the acid in each pan in small quantities at a time. An aluminium fork is used for the purpose. When the charge of cotton waste has been dipped, perforated earthenware plates are placed on the top of it, to keep it all under the surface of the acid; a film of cold water is run on to the surface of the plates, and serves as a seal to prevent fumes getting into the room, and the aluminium hoods are removed. The cotton waste remains soaking in the acid for two and a-half hours; at the expiration of that time its conversion to guncotton is complete. The cock leading to the waste

acid pipe is then opened, and the waste acid allowed to flow away from the guncotton at a definite rate, whilst cold water is allowed to flow on to the top of the perforated plates at an equal rate. The water follows up the acid through the guncotton without any appreciable mixing of the water and the acid taking place, and when the whole of the acid has been displaced in this way, the water is allowed to drain away from the guncotton, which is then ready for the final purification process. This system of manufacture possesses many advantages over the systems which it is superseding. Foremost among them are:—

1. Decreased cost of manufacture, due to the facts that for a given output very much less labour is required; that the plant is both very cheap and very durable; that no power is required to work it; that less acid is lost in the washing processes; and that, owing to the absence of fumes and spilt acid, the cost of maintenance of the buildings is reduced.

2. Increased safety as far as personnel is concerned, because there is no escape or splashing about of acid, which in the old processes was a fruitful source of acid burns, and also because decompositions, which used to take place both in the digesting pots and in the acid centrifugals, with the consequent evolution of poisonous oxides of nitrogen, no longer occur.

3. A better guncotton is obtained. It is freer from unconverted cotton, and as the whole of the nitration and preliminary washing operations are carried out in earthenware receptacles, it is freer from mineral impurities.

4. An increased yield to the extent of about 7 per cent is realised.

The manufacture of guncotton was not commenced at the Royal Gunpowder Factory, Waltham Abbey, until the year 1872. Shortly after that date an improvement was made in the purification process. It consisted in subjecting the guncotton, while still in the waste form, to a series of steam boilings in large wooden vats. In the early days of this process boilings of long duration were used throughout. Later, a system was introduced in which a large number of short boilings at the commencement was followed by a couple of final long boilings. With the introduction of the displacement process of nitration, a thorough investigation of the chemistry of the boiling process was undertaken at Waltham Abbey, and as a result it was ascertained that a more rapid purification was effected by means of two long boilings, each of twelve hours duration, followed by a series of very much shorter ones.

It is very probable that the displacement system of nitration is itself responsible for the reduction in the amount of boiling required to produce a stable guncotton. Although there is no appreciable amount of mixing taking place between the displacing water and the waste acid, still mixing at the surface of contact does occur to a slight extent, sufficient to produce a distinct rise of temperature. The zone of warm acid liquid produced passes very slowly through the whole of the guncotton, removing in its course various impurities. The purifying action of this liquid is no doubt due to the fact that it possesses strong oxidising and solvent properties.

The pulping process introduced by Abel is still universally employed, and although its value from a purification point of view is no longer of such great importance now that guncotton is boiled, as it was in the early days of cold water washing, it is undoubtedly still of use in effecting a final purification of the guncotton.

In the beating engine, the mechanical process of reducing the guncotton to a pulp is effected, but no actual removal of impurities takes place, because the water is not changed during the operation. The impurities still present in the guncotton at this stage are both mechanical and chemical. The mechanical impurities consist chiefly of particles of metal of various kinds, sand and fine grit, wood, and similar substances, introduced originally in the cotton waste and during the processes of manufacture. The chemical impurities are bodies produced by the action of the nitrating acid on bodies other than cellulose; they are

not entirely removed in the boiling process, but are set free in the pulping. To remove the mechanical impurities the guncotton pulp in a large volume of water, is at Waltham Abbey run from the beaters over flannel laid on long shallow troughs, the troughs having pockets with baffle plates at intervals. The rough surface of the flannel retains the fine particles of grit, &c., and the larger particles settle in the pockets or grit-traps. In the last pocket an electro-magnet is inserted to remove iron or steel particles, which may have escaped retention in the grit-traps.

The guncotton thus freed from mechanical impurities runs into large oval iron tanks, called "poachers," where it receives several cold water washings. The contents of the poacher are agitated by means of a power-driven wooden paddle-wheel, and then allowed to settle. The washing water containing the impurities is drawn off from the surface of the guncotton by means of a large skimmer, in order that not only impurities in solution may be removed, but also any light solid impurities in suspension.

The finally purified pulp is passed to a moulding machine, where it is lightly compressed to remove the bulk of the water, and converted into a form in which it can be easily handled. If intended for use in mines or torpedoes, or for demolition purposes, the lightly compressed shapes are submitted to heavy hydraulic pressure, converting them into dense hard blocks.

The other high explosive of which I am to speak, viz., nitroglycerin, enters into the composition of many modern propellants. Nitroglycerin was discovered by Sobrero in 1847, but it remained for a long time a chemical curiosity only.

Alfred Nobel commenced its manufacture as a blasting agent, about 1868, for which purpose he absorbed nitroglycerin with an infusorial earth, known as kieselguhr, and gave the compound the name of dynamite. But, prior to this, nitroglycerin had been made on a large scale in America, where it was frozen after manufacture, for purposes of transport, and used for blasting.

Nitroglycerin is a liquid, and is a much more violent explosive than guncotton, and whereas the manufacture of guncotton is absolutely safe throughout, that of nitroglycerin is dangerous. The risks attendant on the manufacture of nitroglycerin are due to the facts that the temperature resulting from the chemical reaction is not so easily controlled and that nitroglycerin, being a liquid insoluble in water, the processes after nitration have to be carried out with a substance not rendered inert, as guncotton is, by admixture with water. For these reasons the nitration of glycerin in the early days of the production of nitroglycerin on a manufacturing scale was carried out in very small quantities.

With the introduction of dynamite, the small pots used for the nitration of glycerin, standing in vessels full of ice-water, were replaced by lead tanks in which considerable quantities of glycerin, amounting to several hundred pounds, were nitrated at one operation. In these vessels the temperature was controlled by means of cold water circulating through lead coils fixed in the tank, and the whole contents of the tank were kept in agitation during the nitration by means of mechanical stirrers, or by compressed air escaping through small holes in lead pipes situated at the bottom of the nitrating vessel. On completion of the nitration it was the practice in the early days to drown the whole of the charge of nitroglycerin and waste acid in a large bulk of water, from which the nitroglycerin separated out, and was removed for subsequent purification by washing with alkaline solutions in lead tanks. This system entailed the loss of the waste acid, and was superseded by a process in which the nitroglycerin and waste acid were run from the nitrating vessel into another vessel termed a separator, and allowed to separate in it. The nitroglycerin, being lighter than the waste acid, came to the top and was run off into a third tank for preliminary purification consisting of several water washings.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 4th, 1909.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

MESSRS. A. G. C. Gwyer, R. E. Jackson, G. T. Morgan, W. N. Morley, C. S. Mummery, C. J. Regan, M. S. Salamon, and A. W. Stewart were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Harry Livsey, 54, Pemberton Street, Old Trafford, Manchester; Robert Cecil Owen, B.Sc., 89, Foregate Street, Chester; Norman Scott Rudolf, M.Sc., Bangalore, India; Henry Llewellyn Smith, B.Sc., 23, Ellingham Road, Shepherd's Bush, W.; Arthur Percy Strohmenger, Bridgebank, Harrow-on-the-Hill; George Bilderbeck Walker, Vale House, Trafalgar Road, Greenwich, S.E.

Dr. DIVERS gave notice that, at the Annual General Meeting of the Society on March 25th next, he would move the adoption of a new By-law, to run as follows:—

XIII. bis.—On Ascertaining the Will of the Society by means of Voting Papers.

The President, either on his own motion or on a written requisition by the Council or by fifty Fellows, shall proceed to ascertain the will of the Society as to any suggested change in the By-laws or in the administration of these laws by the Council, by causing to be delivered, along with the *Proceedings* or separately, a notice to each Fellow of the change proposed, together with a voting paper upon it, to be filled in by the Fellow and returned to the Secretaries not later than a prescribed date. After that date the results of the voting shall be counted by the Secretaries and two Scrutineers, appointed by the President, and be reported by him to a Council Meeting and to a General Meeting, upon which the Council shall proceed to act in accordance with the majority of votes, as being the expression of the will of the majority.

The PRESIDENT read the names of the Fellows recommended by the Council for election as Officers and as Ordinary Members of Council of the Society.

A Ballot for the election of an Honorary and Foreign Member was held, and the PRESIDENT declared subsequently that Prof. Dr. Georg Lunge, of Zürich, had been unanimously elected.

Of the following papers, those marked * were read:—

*56. "*The Action of Fuming Sulphuric Acid on Triphenylsilicol.*" By GEOFFREY MARTIN and FREDERIC STANLEY KIPPING.

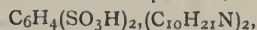
Tetraphenylsilicane is decomposed by fuming sulphuric acid, giving sulphonic derivatives of benzene (Kipping and Lloyd, *Trans.*, 1901, lxxix., 449), and phenylbenzylethylpropylsilicane is decomposed by sulphuric acid, the phenyl group being eliminated in the form of benzene (Kipping, *Trans.*, 1907, xci., 209).

These facts led the authors to doubt the existence of the "triphenylsilicoltrisulphonic acid" recently described by Ladenburg (*Ber.*, 1907, xl., 2274; 1908, xli., 966), and a repetition of his experiments leads to the conclusion that his acid is not only a mixture, but also that it does not contain any appreciable quantity of triphenylsilicoltrisulphonic acid.

Even when triphenylsilicol is treated with fuming sulphuric acid at -10° , the greater part, if not the whole, of the silicol is decomposed and benzenesulphonic acid is formed, whereas at higher temperatures benzenedisulphonic acid is produced; no compound containing silicon was isolated, but evidence pointing to the presence of diphenylsiliconedisulphonic acid, $\text{SiO}(\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H})_2$, in the crude product was obtained.

1-Menthylamine benzenesulphonate, $\text{C}_6\text{H}_5\cdot\text{SO}_3\text{H}\cdot\text{C}_{10}\text{H}_{21}\text{N}$, forms colourless needles, melts at $223-226^{\circ}$, and is readily soluble in water, alcohol, or chloroform, but sparingly soluble in ethyl acetate.

1-Menthylamine benzenedisulphonate,



melts at 212° , and is readily soluble in ethyl acetate, alcohol, or water, but insoluble, or nearly so, in ether.

*57. "*The Ignition-temperatures of Gases.*" By HAROLD BAILY DIXON and HUBERT FRANK COWARD.

The temperature to which two gases must be heated in order that, when brought into contact, they will inflame immediately has been determined by passing an inflammable gas up a tube, terminating in a nozzle, fixed in the centre of a second tube conveying a current of air or oxygen, and electrically heated. Thus no reaction occurred during the preliminary heating of the gases. The temperature of the gas 2 mm. below the nozzle was measured by means of a protected thermo-junction.

The ignition-temperature of hydrogen thus obtained was constant, within 10° , under variation of the following circumstances:—

1. The rates of flow of the gases, within wide limits.
2. The size, material, and surface condition of the jet and of the walls of the furnace.
3. The rate of heating of the furnace.
4. The position of the thermo-junction, either inside or just outside the nozzle.

The ignition-temperature was at first decreased some 20° by increasing the diameter of the outer tube, but a limit was then reached when doubling the diameter produced no further decrease.

The ignition-temperature was raised 5° by working under half an atmosphere pressure, but decreased by 30° under a pressure of two atmospheres.

The ignition-temperature of hydrogen in air is the same as in oxygen.

The results obtained at atmospheric pressure are given in the following table. The paraffins and ammonia gave numbers varying with the rates of flow of the gases, as well as with the size of the furnace tube, so that their ignition temperatures are not so clearly defined as those of hydrogen, carbon monoxide, and the other gases.

Gas.	Ignition-temp. in oxygen.		Ignition-temp. in air	
	Between.	Mean.	Between.	Mean.
Hydrogen	580—590°	585°	580—590°	585°
Carbon monoxide (moist)	637—658	650	644—658	651
Cyanogen	803—818	811	—	—
Ethylene	500—519	510	542—547	543
Acetylene	400—440	428 (?)	406—440	429
Hydrogen sulphide	220—235	227	346—379.	364
Methane	556—700	—	650—750	—
Ethane	520—630	—	520—630	—
Propane	490—570	—	—	—
Ammonia	700—860	—	—	—

DISCUSSION.

The PRESIDENT asked whether the temperature of ignition would not be affected by varying the proportion of the gases; for example, if the rate of flow be so adjusted as to diminish the relative amount of oxygen, while keeping that of the hydrogen constant.

Professor DIXON replied that alteration of the proportion of the gases within wide limits had no effect on the ignition-temperature.

*58. "*The Alkaloids of Senecio latifolius.*" By HENRY EDGAR WATT.

The author has made a chemical examination of *Senecio latifolius* (N.O. *Compositæ*), a poisonous plant which grows in South Africa, collected before flowering and also after flowering, and has isolated two new alkaloids of the formulæ $\text{C}_{18}\text{H}_{27}\text{O}_8\text{N}$ and $\text{C}_{18}\text{H}_{25}\text{O}_7\text{N}$ respectively, for

which the names *senecifoline* and *senecifolidine* are proposed. The proportion of these substances present in the plant before flowering is equivalent to 1.20 per cent, whilst in the mature plant it only amounts to 0.49 per cent.

Senecifoline crystallises in colourless, rhombic plates, which melt at 194–195°, and has $[\alpha]_D + 28.8'$; it forms well-defined salts with nitric, hydrochloric, or hydriodic acids, and also an *aureichloride*. It can be decomposed by alkali into a hitherto undescribed dicarboxylic acid, $C_{10}H_{16}O_6$, which it is proposed to name *senecifolic acid*, and a new base, $C_8H_{11}O_2N$, for which the name *senecifoline* is suggested.

Senecifolidine crystallises in colourless, rhombic plates, which melt at 212°, and has $[\alpha]_D - 13.56'$; it differs considerably from *senecifoline* in other physical respects, and forms salts corresponding with those mentioned above.

DISCUSSION.

Dr. WATT stated, in reply to Dr. Bywaters, that Prof. Cushny had kindly undertaken to work out the pharmacology of the alkaloids, and had already reported that one of them was poisonous to animals.

*59. "An Interpretation of the Hantzsch-Werner Hypothesis." By MARTIN ONSLOW FORSTER and FREDERICK PERCY DUNN.

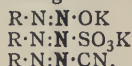
From an investigation of the behaviour towards diazomethane displayed by some typical oximes, the authors were led to suggest a possible explanation of the stereoisomerism occurring in this group of compounds.

DISCUSSION.

Dr. FLÜRSCHHEIM suggested that Dr. Forster's interesting hypothesis might perhaps also apply to the diazo-compounds formulated by Hantzsch as *syn*- and *anti*-isomerides.

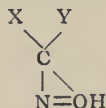
Dr. MORGAN remarked that it would be of interest to know whether the supplementary valencies referred to by Dr. Forster were the ordinary valencies of oxygen and nitrogen indicated by the position of these elements in the periodic classification or the more elusive "Nebenvalenzen" postulated by Werner.

On the ordinary theory of valency, the isomeric diazo-derivatives fall into line with this conception of the structure of the *syn*- and *anti*-oximes, for the former series of isomerides contains the necessary grouping with an element of variable valency (shown in heavy type) contiguous to the double linking—



In the third case the required supplementary valencies could be obtained by a rearrangement of the cyanogen group.

Mr. BALY asked Dr. Forster whether he had considered the expression—



as the extreme phase arising from his formula. This would make the oxygen atom quadrivalent, but there appears to be no objection to this, seeing that Dr. Forster's own formula postulated a valency on the part of the oxygen supplemental to the two normal valencies. Dr. Forster's formula, moreover, would seem to require a supplemental valency on the part of the carbon in addition to the normal four.

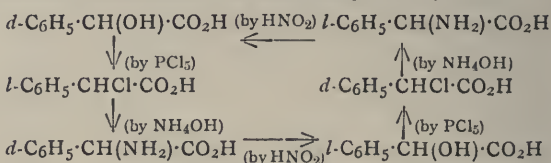
*60. "The Triazo-group. Part IX. Transformation of Cinnamoylazoimide into Cinnamenylcarbimide (cinnamenyl isocyanate)." By MARTIN ONSLOW FORSTER.

The production of cinnamenylcarbimide when cinnamoylazoimide loses nitrogen in absence of water leads to the conclusion that other acyl azides owe their property of giving carbamates and carbamides with alcohols and amines respectively to intermediate formation of the respective carbimide.

*61. "Experiments on the Walden Inversion. II. The Interconversion of the Optically Active Mandelic Acids." By ALEX. MCKENZIE and GEORGE WILLIAM CLOUGH.

The preparation of *d*-phenylchloroacetic acid was described.

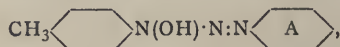
The following points have been investigated: action of water on *l*-phenylchloroacetic acid, action of water on salts of the optically active phenylchloroacetic acids, the displacement of chlorine in the active phenylchloroacetic acids by the amino-group, and the displacement of the amino-group in the active phenylaminoacetic acids by the hydroxyl group and by halogen groups. The inter-conversion of the active mandelic acids can be effected by a method different from that described previously, thus—



The striking feature in each one of these changes is the large amount of racemisation which always occurs.

62. "Diazohydroxylamino-compounds and the Influence of Substituting Groups on the Stability of their Molecules." By NORMAN LESLIE GEBHARD and HERBERT BRYAN THOMPSON.

Arylhydroxylamines react with diazonium salts to form diazohydroxylamino compounds or azohydroxylanilides, a class of substances which may be looked upon as hydroxyl derivatives of the diazoamino-compounds, in which the imino-hydrogen atom of the latter is replaced by a hydroxyl group. The tautomeric phenomena shown by unsymmetrical diazoamino-compounds is not observed with the diazohydroxylamino-compounds. A series of these substances, derived from *p*-tolylhydroxylamine and various diazonium compounds, has been prepared with the object of examining the general properties of these little-known substances, and comparing the various compounds prepared with one another, with the view of determining the effect of substituting groups of various types and in different positions in the molecule on their general stability. The parent substance was benzenediazohydroxylamino-*p*-toluene—



and a number of derivatives of this containing various substituting groups in the ring A have been prepared. The substituting groups used were methyl-, bromo-, nitro-, and carboxyethyl, whilst attempts were made to prepare the corresponding sulphonic acid and hydroxyl derivatives.

63. "Tetraketopiperazine." Part II. By ALFRED THEOPHILUS DE MOULPIED and ALEXANDER RULE.

The authors described the preparation and some of the reactions of tetraketopiperazine in a previous paper (*Trans.*, 1907, xci., 176). Attempts have since been made to reduce the compound to a piperide derivative, but without success. Phosphorus pentachloride and phenylcarbimide are without action on the tetraketone.

The formation of coloured compounds during the preparation of the tetraketone had been noticed, and these are now found to be additive compounds of the sodium salt of tetraketopiperazine with sodium alcoholates.

They vary in colour from deep indigo-blue to bright purple, and are easily decomposed by water, but remain unchanged in dry ether.

64. "The Miscibility of the Pyridine Bases with Water and the Influence of a Critical-solution Point on the Shape of the Melting-point Curve." By OTTO FLASCHNER.

The problem of the connection between chemical constitution and mutual solubility of two liquids has been investigated in the case of the members of the pyridine and

piperidine series combined with water. The width of the solubility ring for partly miscible liquids is taken as a comparable measure of the miscibility, whilst the miscibility of completely miscible pairs is defined by the width of that negative solubility ring which is obtained under a certain external influence, such as pressure or the solution of a third substance. The amount of this external action to be measured is that required to bring about under normal conditions the first appearance of two liquid phases. These considerations are illustrated by the miscibility of the three picolines and pipicolines with water.

The influence of the neighbourhood of a critical-solution point on the shape of the melting-point curve was discussed, and in the solutions of the zinc double salt of γ -picoline in the different aliphatic alcohols was found a convenient series of examples by means of which the analogy between the shape of a melting-point curve and that of an isotherm of a vapour in the neighbourhood of the critical point can be demonstrated.

65. "The Preparation of Dichlorocarbamide." By FREDERICK DANIEL CHATTAWAY.

When dichlorocarbamide is prepared by passing chlorine through a cooled concentrated aqueous solution of carbimide, a yield of about 25 per cent of the theoretical can with care be obtained. Unless, however, the process is very rapidly carried out, with efficient cooling, the quantity which separates falls much below this maximum. The loss is mainly due to hydrolysis of the dichlorocarbamide under the influence of the hydrogen chloride formed in the substitution. If this hydrogen chloride is removed immediately it is formed by combining it with some basic substance, hydrolysis is to a large extent prevented, and, if suitable quantities are used, over 75 per cent of the amount of dichlorocarbamide theoretically obtainable from the carbimide used can be isolated in a pure dry state.

Details of the procedure recommended, in which the hydrogen chloride is removed by zinc oxide, were described.

66. "Thiotetrahydroquinazolines, Methylenecarbamides, Dicarbaniinomethylenediamines and their Homologues." By ALFRED SENIER and FREDERICK GEORGE SHEPHEARD.

The interaction of arylthiocarbamides with arylmethylenediamines at temperatures from 150° to 200° results in the formation of cyclic compounds: cyclic carbamides and quinazolines. When the para-position in the aryl group of either the diamine or the thiocarbamide, or both of them, is occupied, thiotetrahydroquinazoline derivatives and diarylthiocarbamide are formed. In all other instances, using thiocarbimides, and in all instances where the oxygen analogues, carbimides, are employed, the experiments being conducted at the temperatures mentioned, unstable cyclic methylenecarbamides or thiocarbamides are probably formed, and at the same time a diarylcarbamide or thiocarbamide. That these unstable cyclic carbamides are actually formed, although they were identified only by the products of their hydrolysis, is rendered extremely probable by the fact that in two instances, employing a different reaction, namely, the substitution of methylenedianiline for a methylenediamine, the authors succeeded in isolating them and proving their instability.

At the ordinary temperature, the course of the reactions is in agreement with previous experiments; carbanilino- or thiocarbanilinomethylenediamines or their homologues are always formed (Senier and Goodwin, *Trans.*, 1901, lxxix., 254; 1902, lxxxi., 283).

67. "The Distillation of Butter Fat, Cocoanut Oil, and their Fatty Acids." By KENNETH SOMMERVILLE CALDWELL and WILLIAM HOLDSWORTH HURLEY.

The authors are of opinion that fats and fatty acids have no boiling-points in the vacuum of the cathode light, but that for any particular substance a temperature can be selected at which evaporation occurs at a speed convenient for fractional distillation.

Butter fat, cocoanut oil, and their fatty acids were dis-

tilled in the vacuum of the cathode light. The lowest fraction obtained from butter fat distilled with the bath temperature at 250–270° and inner thermometer at 187–210°. Tributyrin distils rapidly with the bath temperature at 127° and inner thermometer at 107°. For this and other reasons, it is concluded that butter does not contain tributyrin. The iodine numbers yielded by the various fractions seem to indicate that there is little or no triolein in butter fat. Lauric acid forms at least 60 per cent of the fatty acids in cocoanut oil, whilst it could not be detected in butter; this method of distillation enabled the authors to detect with ease the presence of 10 per cent of cocoanut oil in butter. The presence of palmitic acid in cocoanut oil has been questioned by Ulzer (*Chem. Revue*, 1899, 203), but the authors isolated several grms. of this acid from cocoanut oil.

68. "Note on the Detection of White or Ordinary Phosphorus in the Igniting Composition of Lucifer Matches." By THOMAS EDWARD THORPE.

As the White Phosphorus Matches Prohibition Act, 1908, will throw upon Officers of Customs and the Inspectors under the Factory and Workshop Act, 1901, the duty of sampling importations of matches and of materials in use in match factories, the author has examined the methods by which the presence of ordinary phosphorus in the igniting composition of lucifer matches containing phosphorus sesquisulphide may be established, and he finds that the most direct and most certain test is to isolate the phosphorus as such, which is conveniently effected by gently heating the composition in a vacuum, when the phosphorus sublimes, and may be readily recognised by its physical characteristics.

69. "Intramolecular Re-arrangement of the Diphenylamine Sulphoxides." (Preliminary Note). By EDWARD DU BARRY BARNETT and SAMUEL SMILES.

When the yellow tetranitro-, 3 : 9-dinitro-, and isodinitro-diphenylamine sulphoxides are treated with suitable reagents—for example, an alcoholic solution of hydrogen chloride—brick-red or chocolate coloured crystalline substances are formed. According to the conditions of the reactions, the dark coloured compounds so obtained are either isomeric with the sulphoxides or differ from them by the content of a molecule of water. The evidence hitherto collected shows that these substances, although they are not of pronounced basic character, contain the orthoquinonoid sulphonium structure, and this view is confirmed by the fact that the unsubstituted diphenylamine sulphoxide is readily converted by aqueous acids into salts of phenazothionium. The depression of the basic properties in the nitro-derivatives is explained by the influence exerted on the quadrivalent sulphur by the acidic substituents.

70. "A Crystalline Bleaching Powder." By KENNEDY JOSEPH PREVITÉ ORTON and WILLIAM JACOB JONES.

A basic hydrated compound of calcium chloride and calcium hypochlorite, which separates on cooling moderately concentrated (about 2N) solutions of bleaching powder, was described. This substance has been obtained in large prismatic crystals, the properties of which closely resemble those of bleaching powder. On the other hand, from very highly concentrated solutions of bleaching powder (about 4N), a hydrated calcium hypochlorite separates at low temperatures.

71. "The Action of Carbon Dioxide on Nitrites." By ERNEST ROBERT MARLE.

The contradiction in the results obtained by Marie and Marquis (*Comptes Rendus*, 1904, cxxxviii., 367), and Meunier (*Comptes Rendus*, 1903, cxxxvii., 1264; compare also Papasogli, *Gazzetta*, 1881, xi., 277; Moody, *Proc.*, 1903, xix., 240) in investigating the action of carbon dioxide on nitrites seems to be partly due to the unsuitability of potassium iodide and starch as a test for traces of nitrites unless special precautions be taken.

Warington (CHEMICAL NEWS, 1885, li., 39) finds that one of the most delicate tests for nitrous acid is the coloration produced with α -naphthylamine (Griess).

Carbon dioxide, prepared from marble and hydrochloric acid, was washed by passing through water in two Drechsel bottles, and was then passed through 10 per cent aqueous potassium nitrite in a Cloez washing bottle, the construction of which is such that it is unlikely that liquid will be mechanically carried over by the stream of gas. It was then passed into water or potassium carbonate for periods varying from one to six hours.

In every case the coloration with potassium iodide and starch seemed slightly greater than that produced by the reagents alone. With α -naphthylamine, a faint pink coloration resulted after a few minutes.

To guard against the possibility of mistaking nitrite, mechanically carried over, for nitrous acid, a dry Arnold absorption apparatus was inserted between the Cloez bottle and the final flask. A slight mist appeared on the inside of the absorption bulbs, which, when washed out with water, proved faintly acid to litmus, and with α -naphthylamine gave a full red colour, appearing in about three minutes. The water in the final flask was neutral (after boiling), and gave with α -naphthylamine, a faint coloration, appearing in about fifteen minutes.

From the data in Warington's paper, the quantity of nitrogen (as nitrous acid) removed by 1 litre of carbon dioxide is probably less than one two-hundredth of a mgrm. The reduction of very dilute potassium permanganate by the solution in the final flask leads to a similar figure.

72. "Estimation of Primary, Secondary, and Tertiary Amines." (Part I.). By JOHN JOSEPH SUDBOROUGH and HAROLD HIBBERT.

The method outlined by the authors some years ago (*Proc.*, 1904, xx., 165) for the estimation of primary, secondary, and tertiary amines has been found capable of general application. Phenetole may be substituted for amyl ether as solvent. The procedure was identical with that followed by the authors in the estimation of hydroxyl groups in carbon compounds (*Trans.*, 1904, lxxxv., 933).

Quantitative results have been obtained with the following substances:—Phenyl- α -naphthylamine, phenyl- β -naphthylamine, $\beta\beta$ -dinaphthylamine, diphenylamine, ethylaniline, methylaniline, β -naphthylamine, p -toluidine, p -chloroaniline, dimethylaniline, diethylaniline, and tetramethyl- p -diaminodiphenylmethane.

73. "The Condensation of Ketones and Aldehydes with the Sodium Derivative of Ethyl Cyanoacetate." By WALTER NORMAN HAWORTH.

The author discussed the nature of the condensation of ethyl cyanoacetate with certain representative aldehydes and ketones.

74. "Experiments on the Constitution of the Aloins." (Part I., Preliminary Note). By ROBERT ROBINSON and JOHN LIONEL SIMONSEN.

In view of the recent publication of a memoir by Oesterle and Tisza (*Schweiz. Wochschr. Chem. Pharm.*, 1908, xli., 701) on the subject of rhein, the authors communicated some of the results obtained during the last two years in connection with an investigation of the constitution of the various aloins, and undertaken with the permission and assistance of Dr. Jowett.

The oxidation of the acetyl derivative of barbaloin with chromic acid leads to the formation of *diacetylrhein*, $C_{14}H_5O_2(OAc)_2 \cdot CO_2H$ (m. p. 245°), and other substances. The investigation and analysis of rhein and its derivatives have conclusively shown that this substance has the composition $C_{15}H_5O_6$, and is a *dihydroxyanthraquinone-carboxylic acid*.

This view is based on the following facts:—I. The substance has all the properties of an acid, and is soluble in the alkaline carbonates and even in sodium acetate. It yields a *methyl ester*, $C_{14}H_5O_2(OH)_2 \cdot CO_2Me$ (m. p. 174°),

and *ethyl ester*, $C_{14}H_5O_2(OH)_2 \cdot CO_2Et$ (m. p. 159°), insoluble in cold sodium carbonate.

2. Rhein yields a diacetate, and prolonged treatment with acetylating agents failed to introduce any further acetyl groups.

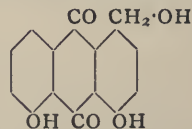
3. Methylation of rhein with methyl sulphate and potassium hydroxide yields *dimethylrhein*, $C_{14}H_5O_2(OMe)_2 \cdot CO_2H$ (m. p. 281–282°), which is also a strong acid, readily soluble in sodium carbonate or sodium acetate, and incapable of acetylation or benzylation. It would appear that the methylrhein (m. p. 288°) which Oesterle and Tisza (*loc. cit.*) describe is identical with this substance, and their observation that it is insoluble in potassium hydroxide may possibly be due to the fact that its potassium salt is very sparingly soluble in potassium hydroxide.

Dimethylrhein yields an *ethyl ester*, $C_{14}H_5O_2(OMe)_2 \cdot CO_2Et$ (m. p. 185–187°).

When treated with thionyl chloride, dimethylrhein yields the corresponding *chloride*, $C_{14}H_5O_2(OMe)_2 \cdot COCl$ (m. p. 190°), which on treatment with concentrated ammonia yields *dimethylrheinamide*, $C_{14}H_5O_2(OMe)_2 \cdot CO \cdot NH_2$ (m. p. 286°).

Now since aloë-emodin is a trihydroxymethylantraquinone and yields rhein on oxidation, it follows that one of the hydroxyl groups is situated in the methyl group, and the authors are therefore of the opinion that aloë-emodin is a *dihydroxyanthraquinolcarbinol*.

The data at present available are not sufficient to prove conclusively the position of the several groups in rhein and aloë-emodin, but there is much reason to believe that rhein is *chrysazincarboxylic acid*, and that the carbonyl group occupies an α -position. The important facts on which these views are based are that barbaloin gives tetranitrochrysazin on treatment with nitric acid, and that aloë-emodin gives α -methylantracene on distillation with zinc dust. If chrysarin is 1:8-dihydroxyanthraquinone, then aloë-emodin would have the constitution—



and rhein would be the corresponding acid.

The authors consider that aloëtic acid, which results from the oxidation and nitration of aloin, is not tetranitroanthraquinone, but dinitrosodinitrochrysazin, and that aloëchrysin, produced by the oxidation of aloin with chromic acid, is the aldehyde intermediate between the primary alcohol aloë-emodin and the carboxylic acid rhein.

75. "The Constituents of Canadian Hemp. Part II. Cynotoxin." (Preliminary Note). By HORACE FINNE MORE.

The aqueous solution of the alcoholic extract of the root of commercial *Apocynum cannabinum* (*Trans.*, 1908, xcii., 1514) yields on extraction with chloroform, after removing the apocynin with ether (*loc. cit.*), a relatively small quantity of an intensely active substance, which produces symptoms identical with those caused by the drug itself.

Cynotoxin, $C_{20}H_{28}O_6$, is a well-defined, colourless substance, which crystallises in small, apparently rhombic pyramids, and melts and decomposes at about 165°. It is sparingly soluble in water and the usual organic solvents, and extremely bitter in taste. Pharmacological investigation by Mr. P. P. Laidlaw, M.B., has shown that it is an extremely potent drug of the digitalis class and that the pharmacological properties of apocynin (acetovanillone, *loc. cit.*) are negligible. The chemical and pharmacological properties of cynotoxin are still under investigation; it is already evident, however, that it is a dilactone, either of Kiliani's digitic acid, $C_{20}H_{32}O_8$ (*Ber.*, 1891, xxiv., 339), or of a closely related isomeride.

PHYSICAL SOCIETY.

Ordinary Meeting, February 26th, 1909.

Dr. C. CHREE, F.R.S., President, in the Chair.

THE meeting was held at the Finsbury Technical College, by invitation of Prof. S. P. Thompson and Prof. E. G. Coker. The new Engineering Laboratory of the College was open to Fellows for inspection.

A paper entitled "*A Laboratory Machine for applying Bending and Twisting Moments Simultaneously*" was read by Prof. COKER.

The present paper describes a machine built by students of the City and Guilds Technical College, Finsbury, in which uniform bending and twisting moments can be applied simultaneously over the whole length of the specimen, and in any desired proportion to each other. The principle of the design is to suspend a rod at two intermediate points by wires depending from a fixed support. The equal overhanging ends of the rod are loaded by weights W , so that the applied couple between the points of support is uniform and of amount Wa , where a is the length of the lever-arm. The rod is also twisted by weights W_1 attached to equal arms of length b , so that there is a uniform twisting moment of amount W_1b between the points of suspension. The two systems of loading are independent, and their ratio can be adjusted to any value desired. The paper then describes in detail the various parts of the actual machine, and shows how the accurate measurement of the strains can be effected. In addition to its applications for bending and twisting, the apparatus may be used for testing a variety of cases of combined stress if a pump is added to give a fluid pressure in the interior of tubes. A test illustrating the failure of bicycle tubing to withstand combined bending and twisting moments was shown at the meeting.

Prof. F. T. TROUTON said he was interested in the experiments from the point of view of the viscous flow which occurred towards the end of the test. He asked if the flow would be different if the end of the bar was unloaded.

THE CHAIRMAN expressed his interest in the paper, and asked if the experiments favoured any particular theory of fracture.

Prof. COKER said he had not yet made many experiments with the machine, but those made seemed to show that failure was due to shear stress. He hoped to carry out further experiments on both ductile and brittle materials.

A paper "*On the Self-Demagnetising Factor of Bar Magnets*" by Prof. S. P. THOMPSON, F.R.S., and Mr. E. W. MOSS, was read by Prof. THOMPSON.

This paper consists of three parts:—I. A discussion of the significance and definition of the self-demagnetising factor of magnets in general, and of bar-magnets in particular; II. A re-determination of the values of the self-demagnetising factor for bar-magnets of circular section; III. Determination of the values of the self-demagnetising factor for bar-magnets of rectangular cross section of various proportions. It is shown that, in general, for every bar-magnet there is a self-demagnetising action the value of which at the middle of the bar depends, for a given intensity of magnetisation, on the length of the bar relatively to its cross section, on the permeability of its parts, and on the distribution of its surface-magnetism. Owing to the circumstance that with every kind of steel the permeability is neither constant nor stands in any simple relation to the flux-density, any calculation of the actual polar distribution for rods and bars is impracticable. The only form of magnet that is practicable for calculation is that of the ellipsoid, the properties of which are that for any and every value of the permeability, and in any uniform field, the surface-magnetism is so distributed that the magnetic force which this distribution exerts in the interior is uniform at every point within, and therefore the internal demagnetising force everywhere within is constant. The

amount of self-demagnetising force per unit of intrinsic magnetisation is recognised as the self-demagnetising factor and has a definite value for ellipsoids of revolution of any assigned ellipticity. In the case of cylindrical bar-magnets the ratio of the net value of the self-demagnetising force for the whole bar divided by the internal magnetisation is called the self-demagnetising factor. The dimension-ratio of a bar-magnet is taken as the length divided by the square root of the cross section. Experiments were first made on the values of the self-demagnetising factor for bar-magnets of circular section, and the results compared with those obtained by Du Bois and Riborg Mann. The values obtained are lower than those found by either of the experimenters named. The determinations were carried down to shorter rods than those examined by either of them, and the discrepancies between their results and the present ones are smaller as the dimension-ratios are larger. It is pointed out that one explanation of the differences may be due to the fact that the magnetising solenoid employed by Riborg Mann was not sufficiently long. Experiments were made to determine the self-demagnetising factor for bar-magnets of rectangular cross section, and it was found that for equal values of the dimension-ratio the factor for bars having a sectional ratio of 2 : 1 was about 93 per cent of that for bars of square section; while for flat bars, having a sectional ratio of 10 : 1, the value of the self-demagnetising factor went down to about 75 per cent of that for bars of square section.

Mr. S. SKINNER said the authors had referred to the ageing of their magnets, but in the actual experiments the field was applied and the measurement taken at once before any ageing could take place.

Prof. F. T. TROUTON pointed out that the self-demagnetising factor became less as the bar became thinner, and asked if this was likely to continue until the bar became a thin tape.

Mr. A. CAMPBELL asked if experiments had been made on different materials. The curves obtained for soft iron might be very different from those obtained for hard steel. With regard to the standard magnet referred to by Prof. Thompson, he had used one at the National Physical Laboratory and found it a satisfactory way of calibrating ballistic galvanometers.

Mr. RAYNER asked if any experiments had been made on hollow magnets, such as those used in the Kew pattern unifilar magnetometer.

Prof. C. H. LEES asked how the iron ring used in their experiments had been prepared, and suggested that it might be advisable to make use of two or three rings.

Mr. R. S. WHIPPLE said the question of the preparation of a standard magnet was an important one. Had the authors made any experiments with ball-ended magnets, especially those with thin wires and large balls?

THE SECRETARY read a letter from Dr. A. Russell, stating that the paper was a notable contribution to the practical theory of magnetism. The authors deserved thanks for their lucid comments on the self-demagnetising factor and for the important experimental results they had obtained. He asked how they had calculated the magnetising force. Had they assumed that the magnetising solenoid was infinitely long and that the radius of the circular axis of the ring was infinite? The errors introduced by these assumptions were small, and Dr. Russell indicated how they might be calculated. It could be shown that if the length of the axis of a helical current was greater than six times its diameter, the magnetic flux entering or leaving the end planes was within about one per cent of half the total flux through the central plane. Seeing that the external field produced by a cylindrical bar-magnet was almost equivalent, except near the ends, to that produced by a helical current, he would not be surprised if the flux leaving the end of a cylindrical bar-magnet was appreciably less than half the total flux through the central plane. He should be grateful if Dr. Thompson could give any data on this point. Further researches on the demagnetising effect of the free magnetism in the air-gap of a split toroid

would be of great interest, and would throw some needed light on the magnitude of the errors involved in the ordinary magnetic formulæ used in engineering.

Prof. S. P. THOMPSON, in reply to Mr. Skinner, said that in their experiments there was an immediate ageing of their magnets on the application of the field. With regard to Mr. Campbell's remarks, different materials would of course give different curves. A forged ring was used in the research, but the forging could not have had much effect on the curves obtained. They had not tested hollow magnets, but experiments had been made on magnets with holes in the ends and the results were similar to those obtained for solid magnets. He had not performed experiments with Robison ball-ended magnets, but the effect of magnetic material at the ends of a magnet was to reduce its self-demagnetising factor. Referring to Dr. Russell's remarks, he said the corrections he mentioned could be neglected.

Prof. S. P. THOMPSON gave an exhibition of the optical properties of combinations of mica and selenite films (after Reusch and others) in convergent polarised light.

Mr. C. R. DARLING exhibited the following:—

An Experiment to illustrate the Temperature of Equal Density of Aniline and Water.—The density of aniline at 0°C . is 1.038, and at 100°C . 0.945, the diminution in density between the two temperatures being practically constant. As the density of water at 100° is 0.959, the temperature-density curves of the two liquids cross each other, showing an equal density at about 63° . By dropping aniline into water at atmospheric temperature, the superior density of the former is shown by the drops remaining at the bottom of the vessel; but when allowed to fall in water at about 80° , the drops of aniline sink until the temperature of the water is attained, and then rise to the surface. By taking a U-tube, with the communicating part of narrow bore, and placing aniline in one branch and water in the other, the aniline column is seen to be shorter at low temperatures; but on surrounding the U-tube with a water-bath and heating, the columns will be seen to be equal in height at 63° ; whilst at higher temperatures the column of aniline is longer than that of water.

A simple form of Thermo-electric Pyrometer for Students' use.—In this instrument the hot junction of nickel and steel, or iron and constantan, is protected by a mild-steel cap, bored from the solid, and about 6 inches in length. This cap is screwed to an iron barrel of any desired length; and the wires pass from the junction through twin-bore fire-clay to terminals screwed into a piece of hard fibre. The terminals are made of the same metal as that of the wire attached, and leads of the same wire are taken to a cold junction, kept in oil, and the indicator. The pyrometer is easily put together by students, and is used to form a temperature-scale from the deflections of a galvanometer by insertion in molten metals, or salts of known freezing-points. The mild-steel cap resists the action of molten substances far better than porcelain or silica, and enables the junction to follow a changing temperature more rapidly. The errors incidental to the forms usually sold, in which no provision is made for a cold junction, are avoided; and no damage ensues from dropping or rough usage, as in the case of pyrometers protected by porcelain or silica. The cap, when worn out, is readily replaced.

A combined Metre-bridge and Potentiometer, with new tapping-key device, for pyrometric and general laboratory work.—The arrangement of this apparatus is that of an ordinary metre-bridge, with four gaps, but with 4 metres of stretched wire; so that 1, 2, 3, or 4 metres of wire may be used in a bridge test. Between each pair of wires is placed a groove, through which passes a rod of phosphor-bronze on which the tapping-key slides. These rods are connected to a terminal at the side: hence it is not necessary to connect directly to the keys. The keys are furnished with two knife-edges, and may be depressed on to the wire on either side of the groove in which they slide, thus facilitating the finding of the balance-point. Each wire is furnished with an arrangement for tightening. The

apparatus may be used as an ordinary bridge, or as a bridge with calibrated wire, it being possible to calibrate any wire by the aid of the others. It may also be used for the measurement of the E.M.F. of thermal junctions, constants of cells, &c., and all the ordinary purposes of a stretched-wire potentiometer.

A new form of Carbon-plate Rheostat, suitable for control of small electric furnaces.—The defect of the ordinary carbon-plate rheostat—difficulty of accurate control when consuming a large amount of energy—is overcome in this instrument by the use of four rows of plates, each 2 inches square, there being 22 plates in each row. Each set of plates is furnished with a separate adjusting-screw, and hence may be kept at different degrees of tightness. By means of simple connecting devices, the plates may be used in series or parallel as desired. This form of rheostat is found to be well adapted for regulating electric-tube furnaces, and for varying the current to any desired extent during the calibration of instruments, &c.

NOTICES OF BOOKS.

Thoughts on Natural Philosophy and the Origin of Life.

By A. BIDDLECOMBE. Third Edition. Newcastle-on-Tyne: R. Ward and Sons. 1908.

THE author of this pamphlet shows himself to be unhampered by conservatism of thought and undeterred by the magnitude of difficulties, and also, we are bound to confess, unfamiliar with the work of his predecessors in the scientific world. He claims to have presented his readers with a new key to the riddle of the Universe, but the most trustful will feel that this key is but poorly constructed to unlock the doors it should enable them to pass through. Platitudes in plenty are to be found scattered through the pages of the book, and many inadmissible generalisations and exaggerations, while some theories which have been suggested previously and, at any rate, provisionally accepted are stated as if they were the product of the author's own brain; for example, he appears to be unaware that the idea that the ether is a form of matter is not new. However, it is not impossible that some readers will find intellectual pleasure in following the author's argument, and will, perhaps, thus widen their conceptions of the structure of matter and the origin of life.

MEETINGS FOR THE WEEK.

MONDAY, 22nd.—Royal Society of Arts, 8. (Cantor Lecture). "Steam Turbines," by G. Gerald Stoney.

TUESDAY, 23rd.—Royal Institution, 3. "Evolution of the Brain as an Organ of Mind," by Prof. F. W. Mott, F.R.S.

WEDNESDAY, 24th.—Royal Society of Arts, 8. "Afforestation and Timber Planting in Great Britain and Ireland," by J. Nisbet.

THURSDAY, 25th.—Royal Institution, 3. "Aerial Flight in Theory and Practice," by Prof. G. H. Bryan, F.R.S.

— Royal Society of Arts, 4.30. "Native Man in Southern India," by Edgar Thurston.

— Chemical, 4. Annual General Meeting. President's Address, "Elements and Electrons."

FRIDAY, 26th.—Royal Institution, 9. "Recent Results of Astronomical Research," by A. Stanley Eddington, F.R.A.S.

— Physical, 5. "Production of Steady Electric Oscillations in Closed Circuits, and a Method of Testing Radiotelegraphic Receivers," by J. A. Fleming. "Effect of an Air Blast upon the Spark Discharge of a Condenser charged by an Induction Coil or Transformer," by J. A. Fleming and H. W. Richardson. "Action between Metals and Acids, and the Conditions under which Mercury causes Evolution of Hydrogen," by S. W. J. Smith.

SATURDAY, 27th.—Royal Institution, 3. "Properties of Matter," by Prof. Sir J. J. Thomson, F.R.S.

Royal Institution.—On Thursday next, March 25, at 3 o'clock, Professor G. H. Bryan begins a course of two lectures at the Royal Institution on "Aerial Flight in Theory and Practice. The Friday Evening Discourse on March 26 will be delivered by Mr. Arthur Stanley Eddington, on "Recent Results of Astronomical Research"; and on April 2 by Professor Sir J. J. Thomson, on "Electrical Striations."

THE CHEMICAL NEWS.

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THE LEAKAGE OF HELIUM FROM RADIO-ACTIVE MINERALS.*

By the Hon. R. J. STRUTT, F.R.S., Professor of Physics, Imperial College of Science, South Kensington.

IN a paper published in *Roy. Soc. Proc.*, 1908, A., vol. lxxxi., p. 272, I showed that phosphatised bones and similar materials were notably radio-active, and that helium could be detected in them. The quantity of helium found was not, however, uniformly greater in the geologically older materials than in younger ones of equal activity. This was hypothetically attributed to escape of helium in certain cases. I desired if possible to obtain direct experimental confirmation of this conjecture.

It would clearly be impossible to detect leakage of helium from materials such as the mineralised bones, even in a lifetime. For any chance of success it was necessary to have recourse to the ores of uranium and thorium, in which the quantity of helium is something like 100,000 times greater.

The method of experimenting was to place a considerable quantity of the ore (usually a kilo. or more) in a bottle, provided with an exit tube and stopcock, and connected to a mercury pump. The bottle was exhausted and the stopcock closed. After the lapse of a definite interval of time, usually a day or more, a small quantity of oxygen was admitted to the bottle and then collected through the pump, carrying with it any helium which had come off from the mineral. The oxygen was absorbed with melted phosphorus, leaving a small residue of helium, together with impurities. Any hydrogen present in the original gas, which may have been liberated by radio-active decomposition of traces of moisture, was burnt along with the phosphorus, and thus got rid of. The residue was transferred to an apparatus consisting of a McLeod gauge in connection with a reservoir containing charcoal. On cooling the charcoal with liquid air, helium was isolated, and the quantity could be measured. As a test of purity, the spectrum could be examined in the capillary measuring tube of the gauge, using external tinfoil-electrodes.

I was astonished at the quantity of helium observed in the first experiments. It exceeded anticipation by hundreds, or even thousands, of times. I shall not describe the experiments in the order in which they were made, but rather in that which seems to connect them best.

It was found that after a radio-active mineral had been powdered, helium was evolved from it, rapidly at first, then at a diminishing rate. The following observations illustrate this.

A quantity (337 grms.) of monazite from the Transvaal was powdered and passed through a wire gauze sieve of 120 threads to the inch. This took about one hour. Immediately afterwards it was put in a bottle and the air pumped out. The rate of evolution of helium in cubic millimetres per day per kilo. of material was as follows:—

Time (days).	Rate.
0·031	261
0·59	76·6
1·6	17·1
2·6	12·3
4·6	9·57
10·6	4·38
33·0	1·14

The first experiment was made as quickly as possible, helium being collected for one hour. Times are measured

from the moment when the powdering was half completed to half-way through the period of accumulation. Naturally the first rapid variations can only be roughly investigated in this way.

Leakage of helium from this sample is still continuing, and it is intended to watch its future course.

It will be observed that the whole quantity which has escaped while the mineral has been under observation is but an insignificant fraction (probably less than a 500th) of the whole quantity present. (This sample of monazite was very poor in helium, containing only one-tenth cc. per grm.).

Moss (*Roy. Dub. Soc. Trans.*, viii., 153) has observed that quantities up to 1 per cent of the helium contained in a mineral can be liberated by grinding in a vacuum. The present observations show that this is but the first rapid stage of a long continued leakage of helium from the newly created surfaces. The view that heat generated in grinding is the important factor appears untenable; for in that case escape of helium should cease on cooling.

It is uncertain how long this evolution of helium continues; in all probability, however, the period is prolonged; and since the majority of radio-active materials can only be obtained in the form of pieces which have been broken off from their natural home a moderate number of years back, any observations made upon them are inconclusive as to the rate at which helium escapes when they are undisturbed in their original surroundings.

It was found, in fact, that pieces from the same stock of monazite, about the size of a lump of sugar, which had not been fractured since they came into my possession two years ago, evolved helium at the rate of 0·002 cmm. per kilo. of material per diem.

This rate, though quite insignificant in comparison with that exhibited by the powdered material, is much in excess of the probable rate of generation of helium by radio-active change. It follows that the present stores of helium could never have been accumulated had the present rate of evolution prevailed throughout the life-history of the mineral.

With a view to testing a mineral more nearly in its natural condition, experiments were made on thorianite, which occurs in gravels, in detached cubic crystals, washed out of their original matrix. This, too, showed a considerable leakage of helium (0·069 cmm. per kilo. per diem). Tests were made at intervals over a considerable period. The rate was found quite uniform, the volume of helium pumped out being proportional to the time of accumulation. A second collection, made immediately after the first, yielded scarcely anything. It is difficult to account for this large evolution of helium from a mineral so nearly in its natural condition. It was thought possible that an explanation might be found by supposing that the temperature of the laboratory (65° F.) was somewhat higher than that of the natural surroundings of the mineral. The latter must, however, be above the freezing-point; and it was decided to test experimentally the rate of evolution at that temperature. The bottle containing the mineral was kept in ice for some days; under these conditions the helium leakage was reduced to about a quarter of its value at the higher temperature (0·018 cmm. per kilo. per day). This is still greatly in excess of the rate of accumulation.

It seemed possible, though unlikely, that the mineral, when kept in a vacuum, lost helium which it would have retained at atmospheric pressure. To test this explanation, the bottle containing the mineral was left filled with oxygen up to atmospheric pressure. At the close of several days the oxygen was pumped out, and absorbed with phosphorus. The ordinary quantity of helium was obtained, the rate of escape being undiminished.

It was noticed that the surfaces of some of these crystals were somewhat weathered. With the idea that this might determine the escape of helium, another sample of thorianite much fresher in appearance was tested. The rate of evolution in this case was only 0·0127, about one fifth of that observed with the previous sample.

* A Paper read before the Royal Society, January 21, 1909.

The majority of minerals allow water to percolate through them. The effective superficial area must therefore much exceed the external surface.

It is probable that loss of helium occurs from the weathering of these interior surfaces as well as from the external faces of the crystals. Abrasion of the external surfaces by comparatively recent rolling in water-courses may have produced some effect.

Under laboratory conditions the rate of escape of helium from minerals always far exceeds the rate of production by radio-active change. Therefore the conditions under which the life of the minerals has been mainly passed, deep down in the earth, where atmospheric agencies have no place, must be supposed more favourable to retention of helium, for otherwise the present accumulation could never have been formed. The observations here recorded leave little room for surprise that fossilised bones and other materials do not always contain as much helium as would be expected from their radio-activity and geological age.

A SIMPLE LECTURE EXPERIMENT TO ILLUSTRATE SIMULTANEOUSLY THREE STAGES OF OXIDATION.

By JOHN E. MACKENZIE.

It is well known that by heating lead peroxide, PbO_2 , it may be converted into red lead, Pb_3O_4 ; and the latter into litharge, PbO , by further heating. This may be simply and effectively shown in the following way:—

Lead peroxide is sprinkled on to a flat-bottomed porcelain basin so as to form a thin layer. The basin, supported on an ordinary triangular tripod, is heated gently at first, and then strongly by the flame of a Bunsen burner placed



directly under it. After a few minutes the hottest part of the basin is found to be covered by yellow litharge, PbO ; the hot part immediately above the iron triangle by red lead, Pb_3O_4 , and the colder part beyond by unchanged lead peroxide, PbO_2 (*vide* diagram).

The contrast between the yellow, red, and puce coloured areas is very striking, and the experiment is therefore one eminently suitable for lecture demonstration.

Chemistry Department,
University of Edinburgh.

A NEW RADIO-ACTIVE PRODUCT OF THE URANIUM SERIES.

By JACQUES DANNE.

A YEAR ago in Mdme. Curie's laboratory I undertook the separation and concentration of the uranium X contained in 20 kilogrms. of uranium nitrate. While thus engaged I discovered a new radio-active substance which appears to be the immediate parent of uranium X; I propose to give this substance the name *radio-uranium*.

The following are the chief operations which were performed in order to concentrate the uranium X, and by means of which I separated this new substance:—

I removed a large part of the uranium X contained in an aqueous solution of uranium nitrate by repeated precipitations of barium sulphate in the solution. The sulphates obtained were converted into carbonates, and after dissolving these carbonates in hydrochloric acid the ordinary analytical separations were performed. The hydrates resulting from this separation contained a small amount of iron, a larger amount of uranium, and in addition the greater part of the uranium X. The hydrates converted into nitrates were dissolved in acetone to separate the uranium from the uranium X, according to Schlundt and Moore's method. Under these conditions the uranium X and the nitrates are insoluble in acetone. However, a certain amount of uranium X may remain in the solution. To remove it the acetone solution was shaken with a small quantity of freshly prepared ferric hydrate, which fixes the uranium X in solution. The nitrates insoluble in acetone and the ferric hydrate were put together and thoroughly washed with acetone to remove all traces of uranium. These products, dissolved in water, evaporated to dryness and ignited, were taken up by a small amount of hot water to which a little hydrochloric acid had been added.

The product A, insoluble in acidulated water, contained the uranium X; it had an activity equal to sixty-three times that of uranium, and weighed 0.5 gm. As for the product B, obtained by evaporating the liquid to dryness, it contained iron, had an activity equal to 0.51, and weighed 0.4 gm.

In October last year I again examined all the products obtained by the above treatment. One fact in particular attracted my attention, namely, that product B had become ten times more active, and I decided to seek for the cause of this abnormal increase of activity.

After having successively eliminated the possible presence of a radio-active impurity belonging to the actinium or radium series, I was able to prove that this increase of activity was due to the formation of uranium X.

Thus I was able to separate a small quantity of uranium X from product B, and to study the laws of the variation of activity of each of the products resulting from the separation.

Product B dried at 150° was taken up with warm water; the insoluble part, consisting chiefly of iron oxide, formed product B₁; the liquid was shaken with freshly precipitated ferric hydrate; the washed and dried hydrate formed product B₂; finally the evaporation of the liquid to dryness gave product B₃.

I determined the activity of these three substances as a function of the time. The following table summarises the results obtained during the last three months:—

Pro- ducts.	Activities.							
	Dec., 1908.				January, 1909.			
	23.	28.	4.	8.	13.	20.	25.	28.
B ₁	2.21	2.12	1.99	1.92	1.81	1.65	1.53	1.47
B ₂	1.50	1.28	1.03	0.91	0.78	0.64	0.54	0.50
B ₃	1.41	1.68	2.04	2.25	2.51	2.82	3.02	3.13

From these measurements it follows that products B₁ and B₂ have a decreasing activity and product B₃ an increasing activity. Moreover, if the curve representing the logarithm of the activity of product B₂ as a function of

the time is traced, it will be seen that the activity decreases, according to an exponential law, in such a way that the activity diminishes to the half value in twenty-two days. This is the number which expresses the period of the decay of activity of uranium X. As for product B₃, its activity increased in the ratio $\frac{33.5}{1.41} = 2.37$ in an interval of forty-four days.

These results can be explained only by supposing that product B contained the immediate parent of uranium X besides uranium X. The separation process carried out with product B divided the two substances in unequal amounts between the three products B₁, B₂, and B₃. Product B₁ contains radio-uranium with an excess of uranium X, product B₂ contains uranium X with a very small quantity of radio-uranium, product B₃ contains radio-uranium with a small quantity of uranium X.

If the small amount of uranium X contained in product B is compared with the much larger quantity of it, which can be extracted from the original uranium solution, it will be seen that in these conditions radio-uranium is very difficult to separate from uranium.

According to the above results this new substance must be classed between uranium and uranium X. Its presence in this position enables an explanation to be found for certain peculiarities which have been detected during the investigation of the uranium salts.—*Comptes Rendus*, 1909, cxlvii., 337.

CHANGE IN THE SPECIFIC GRAVITY OF CAUSTIC SODA SOLUTIONS.

By CLAYTON BEADLE.

WHEN caustic soda solution of 60° T. made from certain kinds of 70 per cent caustic is diluted to a 16° Tw., rapidly mixed, and cooled to 60° F., the specific gravity is found to gradually increase; the writer first noticed this in August, 1889, when he made a number of observations. Such an observation as this must, it was thought, have been noticed by others, and consequently the writer did not attempt to publish the results. Moreover, the results were shown at the time to several chemists, who discredited them and could not offer any explanation. Since that time the writer has failed to discover any publications on the subject, and therefore ventures to think that these results may be of interest.

It was the duty of one of the workpeople in a large paper mill to reduce a 60° Tw. solution of caustic soda to 16° Tw. by running the stronger solution from a copper to a tank below containing hard water. Immediately on dilution and mixing, a sample was taken out and rapidly cooled to 60° F., and the strength taken with a Twaddell hydrometer. It was found that the solution some time after dilution always read considerably above 16° Tw. Consequently the writer took samples from a mixing, and found that the hydrometer actually rose in the liquid when kept at a constant temperature. The experiments were repeated with a specific gravity bottle, when it was clearly demonstrated after filling the bottle that the liquid gradually underwent a contraction.

The following titrations show this change:—

Strong Caustic Solution from (70 per cent) Caustic Soda freshly Diluted to 16° Tw. at 60° F.

	Methyl-orange.	Litmus.	Sp. gr. by bottle.
	Per cent.	Per cent.	Per cent.
	6.045	5.636	
6 hours after	6.450	6.430	

A Mill Sample at 15° Tw.

	5.332	5.316	1.0747
35 minutes after	5.378	5.388	1.0752

One important fact will be noted here which might assist in an explanation. The titration with litmus is lower than with methyl-orange to begin with, but a point is reached in time where the two titrations come very close together. The caustic soda used contained a considerable quantity of alumina, and the water used for its solution contained 21° of hardness, due chiefly to bicarbonate of lime, being practically of the same composition as that supplied by the then Kent Water Works Co. On dilution always a certain quantity of alumina was found to rise to the surface as scum. If the dilution was made with distilled water, no separation of alumina took place.

The following is an analysis of the incrustation formed on a galvanised-iron tank in which the 16° Tw. caustic soda solution was stored. This incrustation was formed as the result of the scum produced on dilution as above:—

Ferric oxide		17.0
Calcium carbonate		74.0
Silica		3.8
Organic matter, moisture, &c., by diff.		5.2

100.0

When titrating in presence of methyl-orange, if alumina be present the neutral point is not reached until the alumina is re-dissolved by the acid (*vide* Cross and Bevan, *Journ. Soc. Chem. Ind.*, April 30, 1889, No. 4, vol. viii.; also Robert T. Thompson, *CHEMICAL NEWS*, 1883 and 1884). With litmus, however, the final point is reached when the alumina is precipitated. The latter, however, is not very definite in presence of large quantities of dissolved alumina. The difference between the two titrations may be taken as a rough measure of the amount of alumina. Some 70 per cent caustic soda was at the time of these experiments dissolved in distilled water; a solution of the same having a specific gravity of 1.0317 contained 2.193 per cent Na₂O by litmus titration and 1.868 per cent by methyl-orange titration. The solid caustic contained then an excessive quantity of alumina. On dissolving the caustic to a strong solution and diluting with the hard water some of the alumina is eliminated, and it appeared that the whole of it is eliminated on standing when the strength stood at 16° Tw. The subjoined table gives some further titrations and specific gravity determinations showing a marked increase in concentration on diluting and standing:—

TABLE A.

	Time.	Sp. gr.	Litmus.	Methyl.	Phenols.
January, 1905—					
1.	23rd, 10.30 a.m. .		19.65	19.65	19.0
2.	23rd, 11 a.m. .	1.08456	19.65	19.65	19.0
3.	23rd, 11.30 a.m. .	1.0847	19.65	19.65	19.0
4.	23rd, 1 p.m. .	1.1009	22.30	23.05	21.7
5.	23rd, 3 p.m. .	1.1157	22.8	24.90	22.2
6.	23rd, 4 p.m. .	1.1335	26.8	29.30	26.1
1.	24th, 2.30 p.m. .		19.65	19.70	19.05
2.	24th, 3 p.m. .		19.65	19.70	19.05
3.	24th, 3.30 p.m. .		22.40	23.65	21.85
4.	24th, 4 p.m. .		22.90	24.85	22.35
5.	24th, 4.30 p.m. .		26.8	29.20	26.20
1.	31st, 1 p.m. .		19.65	19.70	19.15
2.	31st, 2.30 p.m. .		19.65	19.70	19.15
3.	31st, 3 p.m. .		22.40	23.10	21.95
4.	31st, 3.30 p.m. .		22.90	25.00	22.30
5.	31st, 4 p.m. .		26.85	29.25	26.15

It may be possible that the sodium aluminate present in solution exhibits a lower specific gravity than the sodium carbonate present after the alumina has separated, but the increase in gravity would appear to be far too great to be accounted for on this basis; unfortunately no complete analysis of the caustic soda in question was made at the time, and the brand of caustic soda that showed this peculiarity is, we fear, no longer available.

A NEW METHOD OF MATHEMATICALLY
HARMONISING THE WEIGHTS OF THE
ELEMENTS, TOGETHER WITH A REVIEW OF
KINDRED WORK,
AND SOME OBSERVATIONS CONCERNING THE
INERT GASES AND SATELLITES.

By F. H. LORING.

IN presenting a new method of harmonising the elements, I purpose at the outset to refresh the mind of the reader by reviewing briefly the previous work. It will be seen that many ideas, advanced from time to time, are to some extent recognisable in the method I have devised.

Many workers in this interesting field have sought to arrange the elements in various ways, with the view to finding some plan or formula which would classify the elements according to their combining weights, or simply express their values by an equation. A considerable degree of success has been achieved, as will be seen from the following brief historic review of the subject.

Probably the first attempt to classify the elements according to their weights was made by Richter (1762—1807), who thought that the combining weights of the bases formed an arithmetical series, whilst those of acids formed a geometrical series. Prout in 1815, and Meinelcke in 1817, regarded the weights as whole numbers and multiples or polymers of hydrogen. Since then others have worked on the same idea, and comparatively recent developments have given some interesting results.*

Döberiner (1817 and 1829) grouped a few elements in "triads." Gmelin, in his "Handbuch der Chemie" (1843), arranged the elements in two ascending rows which formed a broad faced V-figure. Over one limb he placed O, and over the other H, N being placed midway between the other two. F, Cl, Br, and I headed the O-limb, these standing side by side in horizontal alignment. S, Se, and Te formed the next row, and so on.

Pettenkofer (1850) regarded the weights as whole numbers, and, by the addition or subtraction of integers, obtained a series. He thought that similar elements formed an arithmetical series resembling the organic radicals, and Dumas, with a like idea in mind, in 1851 formulated a law to the effect that those bodies having like characteristics will follow a sequence in weight and chemical properties, as instanced by Cl (gaseous), Br (liquid), and I (solid).†

* Bernoulli (*Z. it. Electrochem.*, 1907, xiii., 551) regards the atomic weights as mean values, the elements being a mixture of polymeric forms of hydrogen, just as the vapour of sulphur is regarded as a mixture of molecules S₂, S₄, &c. The author calculates by thermodynamic recurring formulæ the combinations thus possible. The weights need not be integral multiples of H, since the apparent atomic weight of an element may be a kinetic mean value. He gives weights calculated to the third decimal place.

† This principle I have recently extended to include molecular groups as shown by the following table, the regularities of which must be regarded, however, as fortuitous:—

	For- mula.	Mol. wt.	P. x	23. Diff.	P.	W.	Monobasic acids formed.
Nitrogen di- oxide... ..	NO ₂	46.0	46	0.00	2	2.056	HNO ₂ & HNO ₃
Chlorine ...	Cl ₂	70.9	69	1.9	3	3.166	HCl
Chlorine di- oxide ...	ClO ₂	67.4	69	1.5	3		HClO & HClO ₃
Nitrosyl chlo- ride ...	NOCl	65.4	69	3.5	3	2.925	HNO ₂ & HCl
Nitrogen tetr- oxide... ..	N ₂ O ₄	92.0	92	0.01	4	4.112	HNO ₂ & HNO ₃
Bromine ...	Br ₂	159.9	161	1.1	7	7.142	HBr
Iodine dioxide	IO ₂	158.9	161	2.0	7		I & HIO ₃
Iodine mono- chloride ...	ICl	162.4	161	1.4	7		HCl & HIO ₃
Chlorine hept- oxide... ..	Cl ₂ O ₇	182.9	184	1.1	8		HClO ₃ & HClO ₄
Iodine bromide	IBr	206.8	207	0.16	9		HBr & HIO ₃
Iodine tri- chloride ...	ICl ₃	233.3	230	3.3	10		HCl & HIO ₃
Iodine ...	I ₂	253.8	253	0.84	11		HI
Iodine pent- oxide... ..	I ₂ O ₅	333.8	333	0.84	14.5		HIO ₃

Kremers, in 1852, "drew attention to the equivalents of several elements showing difference among themselves approximately equal to 8, and to the fact that the equivalents of some metals (Mg, Ca, Fe) are nearly products of 4 with an odd integer, whilst others (O, S, P, Se, &c.) are products of 4 with an even integer."*

Gladstone, in 1853, published a paper "On the Relation between the Atomic Weights of Analogous Elements." He compares the atomic weights of elements with the molecular weights of organic radicals, and divides the elements into three broad groups:—(1) "Those having the same weight; (2) those whose weights form a geometrical series; and (3) those whose weights form an arithmetical series." Cooke, in 1854, arranged all the elements then known in six series, each of which he reduced to a general formula of this order:— $8+n9$; $4+n8$; $8+n6$; $6+n5$; $4+n4$; and $1+n3$. The first group included O, F, Cl, Br, and I. Lessens, in 1857, arranged the elements in triads, and obtained twenty groups. Strecker, in 1859, called attention to the following series:—Cr 26.2, Mn 27.6, Fe 28, Ni 29, Co 30, Cu 31.7, and Zn 32.5. Lothar Meyer, in 1860, observed (1) "if the elements be arranged in order of their atomic weights, there is a regular and continuous change of valency as we pass from family to family; and (2) "that the successive differences of elements in the same column are at first, approximately, 16, except Be, then they increase to about 46, and, finally, approach a number ranging from 87 to 90." De Chancourtois, in 1862, devised the "Telluric Helix," which is well known. The elements are arranged on a cylinder so as to trace a spiral. Supplementary helices are required to take all the elements. Newlands (1863-64) wrote as follows:—"If elements be arranged in the order of their equivalents, with a few slight transpositions, it will be observed that the elements belonging to the same group usually appear in the same horizontal line. It will be observed that the numbers of analogous elements generally differ by 7 or some multiple of 7." In other words, the members of the same group stand to each other in the same relation as the extremities of one or more octaves of music.†

Mendeleëff, in 1869, first published his Periodic System. This was to some extent foreshadowed by Lothar Meyer, Newlands, Dumas, and others. The work is too well known to need description here. Mills, in 1884, sought to express the atomic weights by the equation $At. wt. = K - 15\beta$. K is practically the number of a series—15, 30, 45, &c.; β is an integer of variable magnitude according to the elements selected, while $\beta = 0.93727$. He divided the elements into 16 groups. Reynolds, in 1886 (see CHEMICAL NEWS, 1886, liv., 1), described a geometrical method of illustrating the Periodic Law by a

It will be seen that practically all the potential acid-forming bodies (in the sense of not possessing hydrogen) which yield monobasic acids at laboratory temperatures tend to exist as stable compounds having a molecular weight that is an approximate multiple of 23. Thorp and Hamby have confirmed the observation of Mallet that hydrofluoric acid is dibasic below 30°. Fluorine does not belong therefore to the series, nor should one expect it to be eligible, since the weight of F₂ is not an approximate multiple of 23. Bodies that conform to this rule fall into periods (P) numbered 2, 3, 4, 5, &c. (W is the weight of the gaseous bodies in grms. per litre at 0° 760 mm. sea-level, lat. 45°, which is of the same order as P being consequent upon the law of Avogadro). This may be taken, notwithstanding the agreements, as an example of chance regularities.

* This I have quoted from Rudorff's "Periodic Classifications," &c. He reviews most of the work done prior to 1900, the date of publication of his book. Reference to papers not described therein will be given in the course of the article. I have made use of his abstracts, but the original papers should be consulted, as it is difficult to do justice to the work in a brief summary.

† Rev. H. G. Wood, of Boston, Mass., in his book, "Ideal Metrology in Nature, Art, Religion, and History" (1908), arranges the elements on what he terms the "geometric scale of doubles." Beginning at 240 for middle C, he has to some extent harmonised the atomic weights by taking tenth parts of the following musical-scale numbers (vibrations) as multiples:—C 240, D 270, E 300, F 320, G 360, A 400, and B 450. For example, $1/10C=24$, $C=12$, $Mg=24/32$, $Ti=48/11$, $1/10C\ddagger=25.6$, $V=51.2$, $1/10D=27$, $Al=27.1$. All the elements are treated in the same manner, giving twelve groupings. The agreements are fairly close, but the elements are not arranged in any known chemical order.

zigzag line, which he subsequently elaborated and described in his Presidential Address to the Chemical Society, March 26th, 1902 (see *Journ. Chem. Soc.*, Part 1, vol. lxxxi.) In his final arrangement he spaced the elements on curves which represent major and minor chord vibrations (stationary waves). The inert gases fell on or near to the nodal points. Tchitchérin, in 1888, working on atomic volumes, proposed the formula—

$$\text{At. vol.} = \text{at. wt.} \times (2 - 0.00535 \times \text{at. wt.} \times N).$$

N is an integer which for Li and Na=8, K=4, Rb=3, and Cs=2. Crookes, in his Presidential Address to the Chemical Society, March 28th, 1888, described a method of classifying the elements in which he afterwards embodies the inert gases (see *Proc. Roy. Soc.*, June 9, 1899). This is a figure 8 in plan, but in perspective it is a single line so looped as to trace a succession of fig. 8's, one over the other. The elements are arranged on equally spaced vertical lines where they intersect the loops. Many elements having like characteristics fall under each other, i.e., in vertical alignment. Stoney, in 1888 (*Phil. Mag.*, 1902, iv., 411), represented the atomic weights as volumes of concentric spheres which are shown on a plane by a system of concentric circles. By introducing equally spaced radial lines, the points of intersection taken progressively, say, in a clock-wise direction, formed a spiral which approximated to one that could be derived from logarithmic or elliptic formulæ. Like elements, except H and He, fall on the same radial lines. Carnelley (1890) gives the formula $\text{At. wt.} = C(M + \sqrt{V})$. M is a term of an arithmetical series depending upon the group to which the element belongs, V is the number of the group, and C is a constant. Adkins, in 1892, builds up the different elements from the series, 7 Li, 9 Be, 11 B, and 12 C, by adding these to numbers: 7, 9, 16, 24, 56, 78, and 94. Rydberg (*Zeit. Anorg. Chem.*, 1897, xiv., 66) shows that the elements from He to Fe approximate to whole numbers, the weights being expressed by the sum of two parts (N+D). Comstock gives a clearly expressed table of Rydberg's system (*Journ. Am. Chem. Soc.*, 1908, xxx., 683). This table I reproduce below with the 1909 weights. N is an integer and D is a fraction, generally positive, and less than unity. If M is the number of the element, then N is equal to 2M for elements of even valency, and 2M+1 for those of odd valency. The following table will make this clear:—

	M.	2M.	2M+1.	At. wt.	D.
He	2	4		3.98	0.02
Li	3		7	7.0	0.0
Be	4	8		9.1	1.1
B	5		11	11.0	0.0
C	6	12		12.00	0.00
N	7		15	14.01	0.99
O	8	16		16.00	0.00
F	9		19	19.0	0.0
Ne	10	20		20.0	0.0
Na	11		23	23.0	0.0
Mg	12	24		24.32	0.32
Al	13		27	27.1	0.1
Si	14	28		28.3	0.3
P	15		31	31.0	0.0
S	16	32		32.07	0.07
Cl	17		35	35.46	0.46
A	18	36		39.9	3.9
K	19		39	39.10	0.10
Ca	20	40		40.09	0.09
Sc	21		43	44.1	1.1
—	22	44		—	—
—	23		47	—	—
Ti	24	48		48.1	0.1
V	25		51	51.2	0.2
Cr	26	52		52.1	0.1
Mn	27		55	54.93	0.07
Fe	28	56		55.85	0.15

Dulk, in 1898, evolved a series of formulæ (derived from geometric figures) two of which are here given:—

$$2 \frac{1}{(1)^2} \cdot \frac{1}{1^2} = 7.0 = \text{Li.}$$

$$2 \frac{1}{(3)^2} + \frac{1}{(3)^4} \cdot \left(\frac{1}{2} \right)^2 = 23.06 = \text{Na.}$$

J. Schmidt (*Zeit. Anorg. Chem.*, 1902, xxxi., 146) calculates the atomic weights of the elements by assigning thereto (except to hydrogen) chemically inactive portions *a*, and assumes that chemical attraction obeys the universal laws of attraction. *b* is the attractive portion. Mono-valent atoms are represented by *a+b*, bivalent ones by *a₁+b₁+b₂*, and so on. Certain assumptions are made, and the calculations are in fairly satisfactory accordance with weight determinations. A. Marshall points out some curious regularities that appear when the atomic weights are referred to other standards than those of O and H (*Chem. Zeit.*, 1902, xxvi., 663, and *CHEMICAL NEWS*, 1902, lxxxvi., 88). For example, when those of Cl, Br, Ag, and I (German Committee weights taken at the time), are multiplied by 2.53868, whole numbers 90, 203, 274, and 322 are obtained. By dividing Li, NH₄, Na, K, and Rb by 1.004, each division gives respectively 7, 18, 23, 39, and 85 exactly, except a small difference in the case of Na. The same factor gives practically whole numbers for Pb, Cd, V, Pt, Sn, Ca, and Al; the factor 1.0551 is given for the Zn—V series. The author connects these regularities with the phenomena of isomorphism. Vincent finds (*Phil. Mag.*, 1902, iv., 103) "that if a list of all the atomic weights in ascending order of magnitude be taken, and the order in this list be called *n*, then the *n*th atomic weight, from *n*=3 to *n*=60, is given by the equation $W = (n+2)^{1.21}$." Iodine is least in agreement by a difference of +3.9. Hughes considers the elements as built up from corpuscles analogous in type to the radicals NH₄, CN, CH, and NH (*CHEMICAL NEWS*, 1903, lxxxviii., 298). Calculations are given. Wetherell takes 4 and multiples of 4, and classifies the elements according to the Periodic System (*CHEMICAL NEWS*, 1904, xc., 260; see also vol. xc., p. 271). He regards the abnormal properties of beryllium (low specific heat, &c.) as due to the presence of a satellite. In the case of Be, the satellite would be relatively large. Te, he suggests, may have a relatively small satellite, and account for the Te—I inversion in the Periodic Table.

Minet (*Comptes Rendus*, 1907, cxliv., 428) assigns to the elements serial numbers, and, by adding six new elements to the series, plots the atomic weights by a curve, $\chi = \chi^{1.215}$. Two modifications of the same order are given. Delauney (*Comptes Rendus*, 1907, cxlv., 1279) finds curious whole-number relations, thus:—

$$C = \frac{12^2}{12}, \text{Zr} = \frac{33^2}{12}, \text{Ce} = \frac{29^2}{6}, \text{and Ti} = \frac{17^2}{6}.$$

More examples of this kind are given.

From the foregoing it will be observed that the methods employed may be classed as—(1) those involving a mathematical treatment without regard to any particular chemical order or classification; (2) those in which the parallel arrangement or gradation of the elements is accomplished, although the mathematical treatment is somewhat imperfect; and finally (3) those involving the calculation of the weights, some useful classification being arrived at at the same time.

While the best general chemical classification of the elements may not accord with their mathematical or geometrical harmonisation, the two ideas are not necessarily opposed. The difficulties are certainly great. But the failure to bring the two methods into perfect accord does not imply that a purely mathematical treatment is not possible. Moreover, a mathematical treatment, if it accords with facts, may lead to new discoveries, and bring to notice other properties than those usually associated with the classification of the elements.

It is with the view of showing a remarkable series of regularities of an apparently *exact* mathematical nature that the plan below given is suggested.

This method is based upon two simple operations. The *first* is to arrange the elements in a regular series, that passes through a zero, according to the empirical equation,—

$$\pm (4P) + K = W;$$

P is a number of an integral series, 0, 1, 2, 3, . . . &c., and K is a constant of somewhat arbitrary selection which, in the calculations here given is 3.1. This equation gives the value W, approximating to the true atomic weight by a plus or minus difference ranging from 0 to 0.9.*

The *second* operation consists in projecting the *differences* between the calculated and actual atomic weights horizontally along a line on which, by the above equation, the element is placed. Referring to the accompanying chart, it will be seen that the elements are first, as it were, hung on the rungs of a ladder, according to their nearness in weight to the values assigned to the rungs by the equation. The ladder passes through a zero, the rungs being four units apart. It should be here noted that, in order to avoid making the letterpress of the tabular part too wide, the names that fall on the same line are shifted to the nearest blank space, and dotted arrows are introduced to connect them with the lines on which they belong.

The final allocation of the elements in the "difference" portion of the chart reveals some chemical regularities, although the true significance of the classification in this respect is not attempted as yet. The alkali metals, except rubidium, fall in the central part of the table, and if the table is folded down the centre on the O-line, so as to superpose the + and - sides, many like elements are brought into approximate line. It is not my present object to attempt any chemical classification, and I do not believe that the system in its present form lends itself to a periodic arrangement worth considering.

Gallium, lutecium, and neoytterbium do not fit into the series as they give differences greater than 0.9. Moreover, their weights are not known accurately to the first decimal place. This may be said of a number of the heavy elements which are included. The chart may, of course, be extended to take radium and uranium.

It is of importance to note that only those elements having certain numerical values fit into the series, and about the same number fall on the positive as on the negative side. The true zero of the system may be taken on the hydrogen line or a fraction of a unit below it. Those elements that fall on the 0.9 line (-) fit also on the 0.9 line (+), and this suggests that such elements should easily change the sign of their valence. Carbon is an example in this respect.

The most interesting part of the table is the elliptical curves which are drawn mechanically, and are symmetrically disposed with reference to the hydrogen line. They are all formed round the common foci (+ +), and spring from the 4-unit lines (where the latter intersect the +0.8 vertical line) on which the elements fall. The curves occur in groups of 9, and intersect practically all the elements. There are two such groups clearly defined. The third is doubtful, as the elements belonging to it would be of very large magnitude, and no accurate determinations are available for the purpose of establishing the curves. The regular manner in which the double curves intersect the elements will be seen from the table (see next column).

In preparing this table, those elements not practically on the curves are moved to the nearest curve. The transpositions are very slight, considering the number of elements involved, and the fact that a number are not accurately known to the first decimal place. To make the

Curve Nos.								
1.	2.	3.	4.	5.	6.	7.	8.	9.
A								Kr
Cl								Ag
Al								Ni
F								Mg
B	Na	Fe	Cu	Br	Co	Sr	As	Si
H	Li	K	V	—	Mn	Se	Yt	Ge
Be (?)	—	P	Zn	—	Rb	Nb	Ru	—
10.	11.	12.	13.	14.	15.	16.	17.	18.
Te								Hg
Rh								Dy
S								Eu
Ca	Ne		I (?)	Xe	Er (?)		Y	Ir
Sc	Zr	Sn	In	La	Tb	—	Sa	Au
Ti	C	Pd	Cd	Mo	Sb	Ce	Tu	—
Cr	O	Ba	Cs	Gd	Pr	Nd	Ta	—

table even more symmetrical, I should be moved to the curve No. 14 and Er to the vacant space on curve No. 16. The table predicts an unknown inert gas, designated by Y, which has been looked for.* The altered atomic weights of some of the inert gases are those kindly given to me by Sir William Ramsay, these being derived from new density determinations. Otherwise the table (chart) is in accord with the International Weights for this year.

The prediction of Y has been arrived at by three more or less independent ways. In the first place, it will be noticed that a circle intersects He, A, and Ne exactly, and also Kr by a correction in the *second* decimal place. These gases, except He, are also intersected by the elliptical curves, and Xe is only a little out. Their position on the curves were noted to be thus:—A first, Kr second, Ne first, Xe second; therefore Y should be first, *i.e.*, not preceded by an element, to preserve the regularity. Referring to the table above, it will be seen that Y should be on the curve with Sa, which is the second element. Assuming that Kr, Xe, and Y might also be intersected by a circle of the same radius as the one that intersects the others, by a trial method I found the position of Y, which coincides with the elliptical curve where it intersects a 4-unit line. The correction of the weights of the inert gases by the "three" intersections gives the following:—

	Observed.	Calculated.	Difference.
He	3.98	3.98	0.00
Ne	20.0	19.999 +	0.00 +
A	39.9	39.90	0.00
Kr	83.0	82.965	0.035
Xe	130.7	130.77	—
Y		174.98	—

Nitrogen and beryllium are the only elements which do not fit into the system. The difference between the observed weight of N and the calculated value for the series is of the order of 1.1. Be falls away from any probable curve. Wetherell (see citation above) has suggested that Be and Te carry satellites, which he suggests would account for the abnormal specific heat of the former and the wrong position of Te with respect to I in the periodic classification. I suggest that Be, N, and I carry a satellite each, which by trial I find to be about 0.2684. Subtracting this figure from N (14.0064) gives 13.7380, which value falls on the first circle. Similarly, assuming Be to be 9.0874 instead of 9.1, and subtracting 0.2684, gives 8.8190, which places Be, minus its satellite, on the first

* Ramsay (*Roy. Soc. Proc.*, Ser. A, Aug. 27, 1908, lxxxi., pp. 178—180) says the Periodic Table shows gaps for two or three inert gases of higher atomic weight than Xe, and an exhaustive search has failed to indicate any new gas, which he says may be due to its instability, like the emanations of radium, thorium, and actinium. Their weights should be about 172, 216, and 260. In the same *Proceedings*, pp. 195—209, Moore reports that he has found no traces of a new constituent of the atmosphere upon careful search, and says that if a new element exists, it must, in all probability, be in less quantities than 1 in 2,560,000,000 parts of air.

* The following examples will suffice to show the development of the series:—

$$\begin{aligned} &+ (4 \times 2) + 3.1 = 11.1 \\ &+ (4 \times 1) + 3.1 = 7.1 \\ &+ (4 \times 0) + 3.1 = 3.1 \\ &- (4 \times 1) + 3.1 = 0.9 \\ &- (4 \times 2) + 3.1 = -4.9 \end{aligned} \quad \begin{aligned} &\text{Positive side (above hydrogen).} \\ &\text{Negative side (below hydrogen).} \end{aligned}$$

curve, and brings the number of elements on that curve to 7, which is in agreement with those on curve No. 10. The weight of Er is doubtful, and it may belong to curve No. 16, in which case I should be on curve 14 to be symmetrical with respect to Br. I therefore propose to assume that the true value for 1, plus the satellite, is 126.963₄ instead of 126.92, bearing in mind that the iodine determinations are not concordant. Subtracting from 126.963₄, 0.268₄ gives 126.6950, which allocates I, minus its satellite, on curve No. 14, and improves the table.

It will be seen that there is a gap in the ninth curve, and it may be wrong to assume that the first and ninth curves should carry seven elements, since, by shifting Al to curve No. 2, and assuming that the ninth curve carries six elements, the elements on the first group of curves will be symmetrically disposed.

While I have gone into the third and fourth decimal place in some of the calculations, this was not done with a view of assuming such a high degree of accuracy as the figures might imply. Indeed, it is probable that the calculations are only approximate at best, and that some of the curves will require shifting, especially since the weights of the elements are not accurate enough to establish the system on an absolute basis. However, the agreements are very close, as will be seen from the following table:—

	Observed.	Calculated.	Difference.
Li.. ..	7.0	7.0	0.0
B.. ..	11.0	10.99	-0.01
C.. ..	12.00	11.999 +	-0.00 +
O.. ..	16.000	16.000	0.000
F.. ..	19.0	19.0	0.0
Na.. ..	23.0	23.005	+0.005
Mg.. ..	24.32	24.285	-0.035
Al.. ..	27.1	27.13	+0.03
Si.. ..	28.3	28.29	-0.01
P.. ..	31.0	30.98	-0.02
S.. ..	32.07	32.055	-0.015
Cl.. ..	35.46	35.45	-0.01
K.. ..	39.10	39.10	0.00
A.. ..	39.9	39.90	0.00
Ca.. ..	40.09	40.075	-0.015
Sc.. ..	44.1	44.09	-0.01
Ti.. ..	48.1	48.105	+0.005
V.. ..	51.2	51.15	-0.05
Cr.. ..	52.1	52.125	+0.025
Mn.. ..	54.93	54.94	+0.01
Fe.. ..	55.85	55.90	+0.05
Ni.. ..	58.68	58.66	-0.02
Co.. ..	58.97	59.00	+0.03
Cu.. ..	63.57	63.53	-0.04
Zn.. ..	65.37	65.34	-0.03
Ge.. ..	72.5	72.59	+0.09
As.. ..	75.0	74.98	-0.02
Se.. ..	79.2	79.25	+0.05
Br.. ..	79.92	79.90	-0.02
Rb.. ..	85.45	85.70	+0.25
Sr.. ..	87.62	87.55	-0.07
Yt.. ..	89.0	89.03	+0.03
Zr.. ..	90.6	90.60	0.00
Nb.. ..	93.5	93.70	+0.20
Mo.. ..	96.0	96.08	+0.08
Ru.. ..	101.7	101.70	0.00
Rh.. ..	102.9	102.83	-0.07
Pd.. ..	106.7	106.76	+0.06
Ag.. ..	107.88	107.90	+0.02
Cd.. ..	112.40	112.47	+0.07
In.. ..	114.8	114.72	-0.08
Sn.. ..	119.0	118.99	-0.01
Sb.. ..	120.2	120.16	-0.04
Te.. ..	127.5	127.50	0.00
Cs.. ..	132.81	132.86	+0.05
Ba.. ..	137.37	137.32	-0.05
La.. ..	139.0	138.94	-0.06
Ce.. ..	140.25	140.22	-0.03

	Observed.	Calculated.	Difference.
Pr.. ..	140.6	140.73	+0.13
Nd.. ..	144.3	144.28	-0.02
Sa.. ..	150.4	150.46	+0.06
Eu.. ..	152.0	152.10	+0.10
Gd.. ..	157.3	157.28	-0.02
Tb.. ..	159.2	159.15	-0.05
Dy.. ..	162.5	162.50	0.00
Er.. ..	167.4	167.51	+0.11
Tu.. ..	168.5	168.57	+0.07
Ta.. ..	181.0	180.90	-0.10
W.. ..	184.0	184.06	+0.06
Os.. ..	190.9	190.50	-0.40
Ir.. ..	193.1	193.05	-0.05
Pt.. ..	195.0	194.60	-0.40
Au.. ..	197.2	197.25	+0.05
Hg.. ..	200.0	199.90	-0.10
Tl.. ..	204.0	204.26	+0.26
Pb.. ..	207.1	206.92	-0.18
Bi.. ..	208.0	208.00	0.00
Th.. ..	232.42	232.54	+0.12
Be.. ..	9.1	9.087	0.012
N.. ..	14.008	14.0064	0.0016
I.. ..	126.92	126.963	0.043
He.. ..	3.98	3.98	0.00
Ne.. ..	20.0	19.999	0.00 +
Ar.. ..	39.9	39.90	0.00
Kr.. ..	83.0	82.965	0.035
Xe.. ..	130.7	130.77	0.07
Y.. ..	—	174.98	—
H.. ..	1.008	1.008 (a)	0.00 (?)

(a) It is impossible to determine the value of this element in the second and third decimal places by the curve drawn.

The agreements between the observed and corrected values are sufficiently close to make the probability of coincidences impossible, when excluding those elements of high atomic weight which are not known with any degree of accuracy. Due allowance should be made for those elements that fall by chance on a curve when it is known that their values are uncertain. In general, the above table may be regarded as good up to cerium, although Dy, Au, and a few others of high magnitude are fairly accurately determined.

It should be borne in mind that a change in the fundamental standards (hydrogen, chlorine, nitrogen, and silver) would involve a re-calculation of many elements, and necessitate a slight general readjustment of the curves. The exact position of the foci and also of the starting-points for the curves—i.e., whether on the 4-unit lines where they intersect the +0.8 line, or at some other point of intersection—can hardly be fixed until all the standards are established beyond doubt.

The accuracy with which the curves are drawn may be judged by their positions with reference to the machine-ruled squares, the chart here shown being a reduction from a drawing 56 cm. × 19 cm., the smallest squares being 1 mm., the next 5, and the largest 10 mm.

7, Doughty Street, London, W.C.,
February, 1909.

Compounds of Gold with Bromine.—Fernand Meyer. —The final product of the action of bromine on gold is pure AuBr₃, easily obtained by shaking the reagents together for long periods, or by heating to 100° and then cooling and repeating this operation many times. AuBr₃ is a black crystalline substance soluble in bromine and volatile in an atmosphere of bromine at 300°. There appears to be no reason for believing in the existence of the compound AuBr₂. At temperatures at which auric bromide dissociates, two compounds, and only two, exist, namely, AuBr₃ itself and AuBr.—*Comptes Rendus*, cxlviii., No. 6.

IMPROVEMENTS IN PRODUCTION
AND APPLICATION OF GUNCOTTON AND
NITROGLYCERIN.*

By Colonel Sir FREDERIC L. NATHAN, R.A.

(Continued from p. 138).

THIS preliminary purification removes most of the free acid adhering to and dissolved in the nitroglycerin, but in order to obtain a stable product a further and prolonged purification is necessary, as in the case of guncotton. This is effected in lead tanks, by repeated washings with warm dilute sodium carbonate solution. The alkali remaining in the nitroglycerin after this treatment is thoroughly removed by washing with purified warm water. As nitroglycerin is a somewhat viscous liquid, special care has to be taken that the washing solutions are brought into very intimate contact with every portion of the charge of nitroglycerin. For this purpose, the method universally employed is to agitate the contents of the washing tanks by means of the escape of air under compression through small holes in the bottom of the tank. As a result of this very thorough agitation, the nitroglycerin, even after the removal, by skimming, of as much as possible of the washing liquid, still contains a small proportion of water suspended in it in a very fine state of division. It also contains small quantities of flocculent impurities and mineral matter derived from the glycerin and acids. To get rid of these bodies, filtration is resorted to; coarse crystalline salt is very usually employed as a medium, but at Waltham Abbey it has been found that a filter in the form of a mat of sponges is more efficacious and free from the objections salt filters possess.

After the removal of the nitroglycerin from the waste acid, which takes place in a comparatively short space of time, the waste acid was run out of the separator into large lead vessels, where it remained for days, in order to allow of the formation and removal of the last traces of nitroglycerin. This process is known as after-separation, and was necessary to enable the waste acid to be dealt with without risk, because as long as it contained any traces of nitroglycerin, it could not be stored or handled, without risk of violent decompositions, or even of explosions, taking place.

This system of manufacture, comprising nitration, separation, preliminary washing, final washing, and after-separation, all carried out in different vessels and in different houses, was the one which, with slight modifications in detail, was followed almost universally, and is still in use in many of the older factories in this country and abroad. Its disadvantages are several. In the first place, owing to the fact that it is unsafe to transport or to carry liquid nitroglycerin about, factories are always designed so that it may flow from process to process by gravity. The result, obviously, is that nitroglycerin houses must be built on the side of a hill, or, as this is not always possible, the alternative of building a nitrating house and also, probably, a separating house, on artificial mounds, has to be resorted to, entailing a very considerable expense.

In the next place, owing to the corrosive nature of the mixture of nitroglycerin and waste acid, and to the acid nature of the nitroglycerin even when separated from the waste acid, the only material which can be used for the cocks necessary to allow of the nitroglycerin and acid to run from vessel to vessel, is earthenware. The use of earthenware cocks is attended with considerable risk, owing to the fact that there is friction in them between the key and the body of the cock; and there is always the risk in moderately cold weather of the nitroglycerin freezing and fixing the key; force, if used under these circumstances, would be very liable to cause accident. Again, the necessity of storing the waste acid under observation for long periods is a costly one, both as regards labour and plant required.

It was to overcome these disadvantages that the whole system in current use for the manufacture of nitroglycerin received very careful consideration at the Royal Gunpowder Factory some years ago.

The first step that was taken to improve matters was to abolish the use of earthenware cocks in the preliminary and final washing tanks. As the nitroglycerin when it was ready to leave these tanks was thoroughly free from acid, it was possible to get rid of the cocks on these tanks, and to replace them by rubber tubes. During the washing operations this tube is secured to a nozzle fixed to the outside of the tank at a point above the level of the liquid. To run off the nitroglycerin it is only necessary to slip the rubber tube off the nozzle and direct it into another vessel or into a lead gutter used to convey the nitroglycerin to the next operation.

Rubber, however, could not be used in the case of the separator or the nitrator, where either acid nitroglycerin, or a mixture of nitroglycerin and acid, had to be drawn off. To overcome the difficulty in this case an entirely new system was invented at Waltham Abbey. Instead of running the nitroglycerin and waste acid on completion of the nitration process into the separator, the separation is allowed to take place in the nitrating vessel itself. Nitroglycerin as it separates from the waste acid comes to the top, it being the lighter of the two liquids, and to remove it from the nitrator all that is necessary is to raise the liquid contents of the vessel gradually until the nitroglycerin reaches the top of the nitrator, where a pipe or gutter is fixed to lead the nitroglycerin away into the preliminary washing tank. This raising of the charge is effected by introducing into the bottom of the nitrator, through the same pipe by which the nitrating acid is admitted, the waste acid from a previous charge. The rate of inflow of the waste acid is regulated so that the nitroglycerin displaced is as free as possible from acid in suspension.

The waste acid has still to be dealt with. It was discovered that the addition of a small percentage of water to this acid, after the nitroglycerin has been separated from in the nitrator-separator, entirely prevents the further formation and separation of the small traces of the nitroglycerin, which the after-separating bottles were required to deal with.

The advantages of the Waltham Abbey plant and system of manufacture over others are briefly as follows:—

1. *Increased Safety.*—By the abolition of all cocks through which nitroglycerin had to pass, the risks attendant on their use have disappeared. By the presence of cooling coils in the one and only vessel in which nitroglycerin and acids are in contact, any undue rise in temperature, always a possibility in the circumstances, can be at once checked. It was not usual to have cooling coils in the separator and after separating bottles.

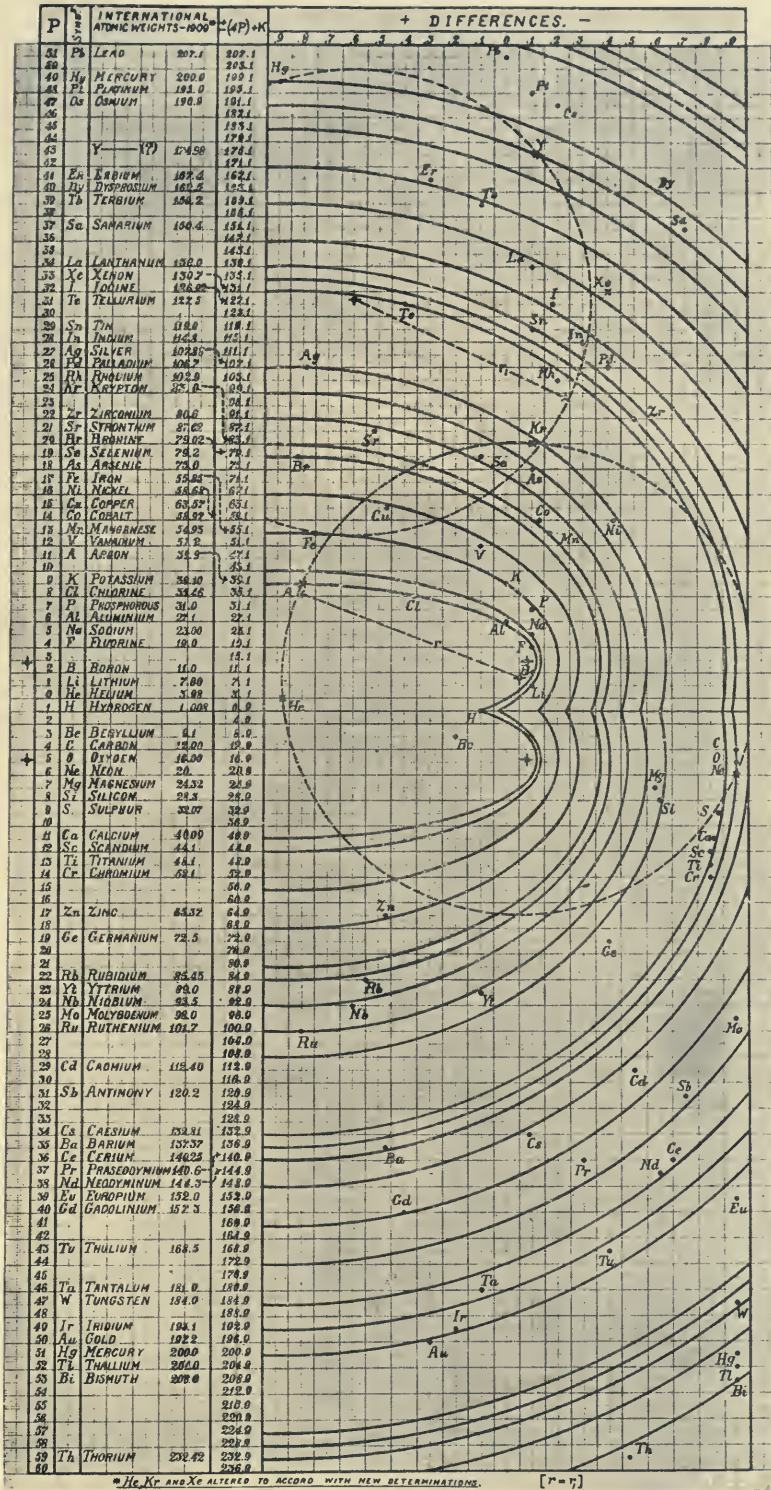
2. *Reduction in Total Elevation for, and Area of a Factory.*—The abolition of the separator, and the running off of the nitroglycerin from the top of nitrator effect a very material saving in the height required.

The after-separating house being no longer necessary, nor the separator house when one existed as distinct from the nitrating house, the number of buildings, and therefore the ground area, is substantially reduced.

3. *Reduced Cost of Production.*—This results from the fact that the capital outlay for a factory is much less, that fewer men are required for a given output, that there is less plant and fewer buildings to maintain, and that the plant suffers slower deterioration. Finally, the yield of nitroglycerin is increased by at least 5 parts for every 100 parts of glycerin nitrated.

The substitution, recently, of Nordhausen for ordinary sulphuric acid, has further improved the yield of nitroglycerin, and whereas a few years ago a yield of 210 parts of nitroglycerin for every 100 parts of glycerin nitrated was considered excellent, the average yield at Waltham Abbey is now 230 per cent, a very high figure in view of the fact that the theoretical yield is 246.74 per cent. The use of Nordhausen sulphuric acid also permits of a considerable

* A Discourse delivered before the Royal Institution, January 29, 1909.



reduction in the proportion of nitrating acid to glycerin, so that a larger output is obtainable for any given sized plant.

In the year 1846, Schönbein discovered guncotton. In the year 1886, that is, forty years later, the French chemist Vieille invented his smokeless powder for military purposes. This explosive, which was primarily designed for use in the small calibre Lebel rifle, consisted essentially of guncotton, and the secret of its success lay in the fact that Vieille so altered its physical state that its rate of combustion, when confined, was under complete control. This condition was arrived at by treating the fibrous guncotton with suitable solvents which entirely destroyed the fibre and converted it into a colloidal horny substance quite devoid of all porosity. The gelatinised guncotton resulting from this treatment burnt, when ignited, from the surface inwards, and by varying the surface area, any required rate of combustion could be obtained. The use of smokeless powders, manufactured in this way, was very soon extended to all natures of ordnance.

The next step in the development of smokeless powders was the combination of nitroglycerin with nitrocellulose. The first powder of this type was the "ballistite" of Alfred Nobel, patented by him in the year 1888. The original ballistite was composed of equal parts of nitroglycerin and of soluble nitrocellulose, a variety of guncotton soluble in nitroglycerin, and no solvent was therefore required in its preparation, although a certain proportion of camphor was used to promote the solution of the nitrocellulose. Another form of nitroglycerin-nitrocellulose explosive is the British service powder, cordite, which originally consisted of nitroglycerin 58 parts, guncotton, insoluble in nitroglycerin, 37 parts, and mineral jelly, a product of the distillation of crude petroleum, 5 parts. To effect the gelatinisation of the guncotton, the solvent acetone, obtained indirectly from the destructive distillation of wood, is employed. The result of subjecting nitrocellulose, in suitable machines, to the action of nitroglycerin or of solvents, of which there are several suitable ones besides acetone, is to destroy its fibre and convert it into a gelatinous mass, in which condition it can be formed into any desired shape. Where solvents are used to produce this result, they remain in the mass during subsequent operations, and are finally driven off by means of heat. The resulting products, somewhat incorrectly termed "powders," which are manufactured in a variety of forms, such as grains and flakes of different shapes, ribbons or strips, solid cords, tubes, &c., vary in consistence with the quantity of nitroglycerin they contain. The more nitroglycerin present, the softer the powder; pure nitrocellulose powders being hard to brittleness.

For practical purposes modern smokeless powders are of two types:—

1. Those consisting entirely of nitrocellulose and termed "nitrocellulose powders."
2. Those consisting of a mixture of nitrocellulose and nitroglycerin, known as "nitroglycerin powders."

Opinions differ somewhat as to the relative merits of these two types; in this country the latter type is preferred. Their characteristic features are, briefly, as follows:—

A nitroglycerin powder is more powerful than a nitrocellulose powder, and the more nitroglycerin present the more powerful the explosive. Therefore, for equal ballistics, a smaller charge of the former than of the latter is required, and, consequently, the chamber capacity and the size and weight of the breech mechanism is reduced; on the other hand, the higher the proportion of nitroglycerin the higher is the temperature of combustion, and the greater the erosive effects on the surface of the bore of the gun.

The presence of nitroglycerin in an explosive allows of the more easy and rapid elimination of the solvent used in manufacture, and of moisture, a small quantity of which is always present in nitroglycerin and guncotton. The sooner this is attained the better, because the longer the time that the powder is being heated in order to dry it, the more likely is its chemical stability to be affected. Moreover, it is a well-established fact that with nitrocellulose

powders it is impossible to remove the volatile matter with anything like the same completeness as can be done in the case of nitroglycerin powders. The consequence is that the slow evaporation from nitrocellulose powders of the residual volatile matter which takes place in store, tends to produce changes in their physical character, and renders them in course of time liable to alter in ballistic properties, and even to develop dangerous pressures in the gun.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, March 12th, 1909.

Dr. C. CHREE, F.R.S., President, in the Chair.

THE following were elected Fellows of the Society:—Prof. P. V. Bevan, J. W. Bispham, L. Blaikie, Prof. E. G. Coker, A. Eagle, Sir R. A. Hadfield, F. J. Harlow, C. F. Hogley, B. M. Narbeth, T. Smith, and Prof. The Hon. R. J. Strutt.

A paper by Mr. A. E. GARRETT on "*The Effect of Radiations on the Brush Discharge*" was read by the Author.

Willows and Peck in 1905 found that radium radiations have the power to extinguish a brush discharge produced by a Wimshurst machine when the gap is greater than 3 to 4 cm. The present experiments show that the same phenomena can be produced by means of an induction-coil capable of giving a 6-inch spark. The observation of Willows and Peck that the β -rays are responsible for the effects produced is confirmed. Experiments are described which illustrate the effect of the nature of the anode on the sensitivity of the positive brush. The appearance of the brush is viewed in a rotating mirror, and also by means of a microscope fitted with a 3-inch objective, and a marked difference is noted between the appearance of a sensitive brush and that of the brush from a pointed anode on which radium has practically no effect. By this means, and also by altering the capacity, it is found that the sensitive nature of the brush depends upon the oscillatory nature of the discharge, and it is thought probable that a side discharge takes place when the brush is extinguished by the radium.

THE SECRETARY read a letter from Dr. R. S. WILLOWS stating that the experiments of the author were the only ones that connected the extinction of the spark with any other feature of the discharge. The most obvious explanation seemed to be that on account of the ionising action of the rays the potential never rose high enough to cause luminescence. This explanation was apparently ruled out by the fact that Röntgen rays do not cause extinction, although the ionisation they produce is much greater than that produced by the radium used. It was thought that the intermittence of the rays was their cause of failure, but it was found that Lenard rays, also produced intermittently, caused extinction. In spite of this difference in the action of Lenard and Röntgen rays the author's experiments showing that the discharge in order to be sensitive must be intermittent, render it probable that the cause of the failure of the Röntgen rays to produce extinction must be looked for in their discontinuous character. Neither the author nor he (Dr. Willows) could obtain a sensitive discharge with a positive point; it was therefore of interest to note that Lebedinsky had recently obtained this by connecting in parallel with a Leyden jar, thus producing the author's condition of a periodic discharge of fairly long period.

Prof. C. H. LEES expressed his interest in the experiments, and referring to the side discharge to the radium, said it was possible that a discharge towards the radium

might be dispersed by the air without giving an actual current from the radium.

Mr. A. CAMPBELL asked what was the frequency of the oscillation in the sensitive brush.

The AUTHOR, in reply to Prof. Lees, said that on several occasions he had detected a slight current from the radium to earth, but the results were so irregular that he omitted them from the paper. With reference to the question of frequency of the discharge producing the sensitive brush, he had compared it with that of a discharge in a hydrogen tube in which the discharge was produced by an induction-coil the primary circuit of which was interrupted by a tuning-fork making 86 $\sim$ per second. The number of images visible in the rotating mirror was in the case of the sensitive brush double that given by the tube, so that the frequency was a very low one.

Mr. A. E. SNOW read a paper on "*Pirani's Method of Measuring the Self-inductance of a Coil.*"

In this method the coil whose self-inductance L is to be measured is joined in series with a condenser of capacity C , and the combination forms one arm of a Wheatstone's bridge. The condenser is shunted by a non-inductive resistance r . The resistances of the other arms of the bridge are adjusted for a steady balance. The result $L = Cr^2$, whence the value found for L is independent of the inductance of the galvanometer, has been proved for the case in which the discharge of the condenser is continuous. In the present paper the case in which the discharge of the condenser is oscillatory is dealt with, the applied E.M.F. being constant. A differential equation of the third order with constant coefficients is obtained from which the value of x —the current passing through the galvanometer—can be found in the form necessary for an oscillatory discharge. It is shown that the discharge of the condenser is of the same nature as that through the galvanometer. The criterion $\int_0^\infty x dt$ is used to express the fact that there is no throw of the galvanometer-needle, the resistance r , or the capacity C being varied until this is obtained. From this the condition $L = Cr^2$ is deduced, so that in the case of an oscillatory discharge of the condenser the value found for the inductance of the coil is not affected by the inductance of the galvanometer.

If the same method is applied to the case of an alternating E.M.F., a result is obtained which involves the inductance of the telephone used to indicate the current. From general considerations this can be shown to be impossible. The method used in the case of a constant E.M.F., therefore, is not available for the investigation of the case in which the E.M.F. is alternating. The difference lies in the fact that the condition for a steady balance is not the same for an alternating E.M.F. as for a constant E.M.F.

Mr. A. CAMPBELL expressed interest in the author's thorough investigation in the first part of the paper. In the case of alternating currents, however, Mr. Snow's final result involved the resistance and inductance of the galvanometer circuit. Since the condition for a balance was that the current through the galvanometer should be zero at every instant, the final result could not involve either of these quantities, both could be altered to any extent without affecting the balance. The correct solution for alternating currents could, however, be obtained without difficulty. Thus, let P be the effective resistance of the coil L , and let $\sigma = A/B$, the rest of the notation remaining unchanged.

Then—

$$P + L\omega\sqrt{-1} + \frac{r}{1 + r^2C^2\omega^2} = \sigma R.$$

Separating the real and imaginary parts,—

$$L = rC(\sigma B - P) \text{ and } rLC\omega^2 = P - \sigma B + r.$$

Hence—

$$L = \frac{r^2C}{1 + r^2C^2\omega^2} \text{ and } P = \sigma B - \frac{r}{1 + r^2C^2\omega^2}.$$

Thus it is seen that the balance depends on the frequency, which must therefore be accurately known in order to determine L and P . Mr. T. Smith had worked out the problem by the author's method, and had found the source of the error. With alternating currents, the initial assumption that the resistances of the four arms are A , B , kA , kB was impossible. When this was put right, B_1 and B_2 both could be equal to zero, which conditions easily reduced to the equations given above.

Dr. RUSSELL pointed out that M. Silva began the investigation of the accuracy of Pirani's method two years ago. He had not, however, discussed the case when two of the roots of the cubic were imaginary. He congratulated the author on having completed Silva's investigation, and said that his solution of the cubic would be helpful in other problems.

The AUTHOR, in reply, thanked Mr. Campbell for his remarks, and said he would make the necessary alterations in the part of the paper dealing with alternating currents.

Mr. W. S. TUCKER read a paper entitled "*Exhibition of a High-potential Primary Battery.*"

The object of the battery is to maintain at known potentials such conductors as the needle of the quadrant-electrometer; for charging condensers in capacity and insulation tests; or for calibrating electrostatic voltmeters. It is composed of a large number of elements in series; the elements consisting of carbon and pure zinc with a nearly saturated solution of calcium chloride as electrolyte. The carbon is a piece of black-lead pencil about 5 cm. long. A strip of zinc-foil about 5 mm. wide is bound to one extremity of the carbon by thin copper wire, and the strip is bent so that its other end nearly touches the carbon of the next element. This contact is just broken by paraffin-wax. The connected ends are melted into a table of paraffin-wax contained in a shallow tray. Elements are mounted in parallel rows—the ends of alternate rows being connected to brass terminals. In the battery exhibited, 900 of these elements are arranged in series. The table of wax with the elements is then inverted, and the exposed ends of the elements dipped in a shallow tray containing the solution, and then withdrawn as quickly as possible. When withdrawn, each carbon-zinc pair is now separated by a layer of solution held in place by capillary effect. The hygroscopic nature of the solution prevents its drying up; and it is found that there is no appreciable chemical waste by local action. When not required for use, the battery can be washed free of the exciting solution and dried.

It is found possible to obtain 1.02 volt per element: so that a total over 900 volts is given. Since the terminals are well insulated, a very steady voltage is obtained, and this has been kept within one-tenth per cent variation for two hours and 1 per cent for half a day—the temperature of the room remaining steady.

The battery has fitted to it an arrangement whereby any desired voltage from that of one to that of all the cells can be obtained by steps of one cell. The last two rows of elements may be introduced at will, and in the last row the elements are each connected to brass studs over which a sliding contact can pass. This contact is connected to the terminal of the battery.

A special feature of the battery is its careful insulation. It may also be mentioned that, should any row of elements get polarised, they gradually recover, apparently owing to the depolarising action of the porous graphite exposed to air.

Mr. F. E. SMITH congratulated the author upon his battery, which he said was small, cheap, and effective. He asked if Mr. Tucker had made experiments with other elements, and whether he had constructed a single cell of low resistance and investigated the change of potential with time.

Mr. A. CAMPBELL asked what happened if the battery was short-circuited, and what determined whether *creeping* would occur when using any particular solution,

Mr. S. G. STARLING said one of the important points about the battery was that it could be washed and put away, and was then ready for use on any future occasion.

The AUTHOR, in reply, said that the only other elements he had used were copper and zinc. He had used different liquids, but always got a lower voltage. Short-circuiting of course caused a fall of potential, but there was not much chemical action on account of the very high resistance of the battery.

A paper "On the Least Moment of Inertia of an Angle-bar Section" was read by Mr. H. S. ROWELL.

The author pointed out that errors in strut design are unavoidably large, particularly those of angle section. Thus an approximate value of the moment of inertia is sufficient. If the mean lengths of the legs are a and b , then θ , the angle which either principal axis makes with the leg of length a , is given by the equation—

$$\tan 2\theta = \frac{6}{\frac{b}{a}\left(\frac{b}{a} + 4\right) - \frac{a}{b}\left(\frac{a}{b} + 4\right)}$$

to a fair degree of accuracy.

If a_1 and b_1 be the outside lengths of the greater and lesser legs respectively, and k the least radius of gyration of the section, then with sufficient accuracy for practical purposes,—

$$\frac{k^2}{b_1^2} = 0.037 + \frac{1.35 \left(\frac{a_1}{b_1} - 1\right)}{100 \left(\frac{a_1}{b_1} - 1\right)^2 + 50},$$

where $\frac{a_1}{b_1} < \frac{5}{2}$.

Dr. RUSSELL expressed his interest in the problem. He suggested that the phrase "second moment of an area" was preferable to "moment of inertia of an area." He asked the author whether he had compared the numbers obtained by his formulæ with the numbers given in manufacturers' catalogues. He noticed that manufacturers introduce corrections for tapering flanges, rounded corners, &c., and that the numbers they gave for the minimum radius of gyration varied largely with the thickness of the web. Large factors of safety were used in practice, but it was highly desirable that the theoretical numbers should be as accurate as possible. Unfortunately, the author had made some approximations which were not really necessary, and these made it difficult to know what weight to attach to his results. Personally he thought that the best way of finding the second moments of angle-bar or other sections was to use an Amsler's integrator. These integrators had been extensively used for many years, more particularly by naval architects, and their accuracy was not inferior to that of graphical methods.

NOTICES OF BOOKS.

Introduction to the Rarer Elements. By PHILIP E. BROWNING, Ph.D. Second Edition. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1908.

A CONCISE account of the methods of extraction and the properties of those elements which are not usually discussed at any length in a general course of inorganic chemistry is given in this book. Some experimental work is described, and many references to current literature and to larger text-books are included. The author has perhaps not been very happy in his choice of material, or rather not judicious in deciding how to apportion out his space. Thus lithium, rubidium, caesium, and beryllium, which are not usually passed over even in fairly elementary text-books, are given

half as much space as all the rare earths together, while platinum again is treated more fully than necessary. Although the second edition has been brought up to date it makes practically no mention of scandium, upon which element very important work was published some months before the book was issued. The additions to the second edition include a fuller treatment of the radio-active elements and also considerable enlargements of the chapter on the rare earths.

The Principles of Inorganic Chemistry. By WILHELM OSTWALD. Translated by ALEX. FINDLAY, M.A., Ph.D., D.Sc. Third Edition. London: Macmillan and Co., Ltd. 1908.

VERY few changes have been made in the third edition of this excellent text-book of inorganic chemistry. Some trifling errors have been corrected, and the additions include a short allusion to the value of the evidence which has been put forward to demonstrate that deviations from the law of conservation of mass are not unknown. A note is also given on the synthetic manufacture of nitric oxide from the air, which at the time of the publication of the second edition had not been performed successfully on a commercial scale.

Untersuchung und Nachweis Organischen Farbstoffe auf Spektroskopischem Wege. ("Investigation and Identification of Organic Dye-stuffs by the Spectroscopic Method"). By JAROSLAV FORMANEK, in collaboration with Dr. EUGEN GRANDMOUGIN. Part I., Second Edition. Berlin: Julius Springer. 1908.

PROF. FORMANEK was a pioneer in applying spectroscopic analysis in the chemistry of dyes and colouring matters, and although many books on the subject have followed the first edition of this work, which appeared nine years ago, it still holds its own among them. However, the very rapid improvement of methods of using the spectro-scope and the large number of data which has been collected by various workers have to a certain extent put the earlier edition out of date, and the time was quite ripe for the appearance of a revision and completion of it. The second edition has been divided into two parts, the first of which is purely theoretical. The introduction explains the foundations of spectroscopic methods, and describes the type of instrument which is most suitable for this class of work. The connections between colour, fluorescence, and absorption on the one hand, and constitution on the other, are next discussed, while in the remainder of the book the author proceeds to the consideration of the individual colouring matters, grouping them together as di- and tri-phenylmethane derivatives, quinonimide and acridine derivatives, and products obtained from anthraquinone. A tabular summary shows clearly the chief characteristics of the spectra of the different compounds, while the spectra of some of the more important substances are reproduced in two plates.

CORRESPONDENCE.

THE INSTITUTE OF CHEMISTRY AND RESEARCH WORK.

To the Editor of the Chemical News.

SIR,—In his Address to the Institute of Chemistry, reported in your issue of March 12 (CHEMICAL NEWS, xcix., 129), Prof. Frankland, F.R.S., referred to "the criticism of the Institute by Prof. Kipping in his Presidential Address to the Chemical Section of the British Association at the meeting last year."

Will you grant me space to point out that Prof. Frankland seems to have entirely misunderstood this "criticism," and

to have drawn from it certain inferences for which there is no foundation.

My suggestion was that the Institute of Chemistry should insist on good research work in the case of all candidates for the Fellowship, so that it would be possible to distinguish between those who are capable routine chemists and those who might be expected to advance pure and applied science.

Prof. Frankland replies that the results of research work are not necessarily recorded in any scientific journal, and that there is a vast amount of research involving originality and attainments of the highest order which from its nature could not be published at all, and then he asks:—"Should chemists who are engaged on such research be debarred from the Fellowship because their names are not at the head of so many dozen pages apiece of the *Journal of the Chemical Society* or in a similar publication?"

Of course not! The very fact that an Associate had shown himself capable of carrying out good original work should forthwith entitle him to demand the Fellowship in accordance with my suggestion.

I need no assurance that Prof. Frankland has "met chemists whose names are not associated with such academic researches, who were nevertheless fully equipped and highly original investigators."

His experience is not unique, but his question, "Should these men not have been admitted to the Fellowship of the Institute?" is again superfluous, as my suggestion was that the Fellowship should be awarded for good original work.

What does Prof. Frankland really mean by these questions? Does he imply that the Fellowship is now conferred on many chemists for original work, and that the adoption of my suggestion would interfere with this practice, or that the Fellowship is now awarded by examination to many who subsequently prove themselves to be fully equipped and highly original investigators? If the former, the implication is obviously groundless; if the latter, it is obviously true; but I would again suggest that the Fellowship should be made a higher honour, and that it should then be awarded *after*, and not before, there is evidence that it is deserved.—I am, &c.,

F. STANLEY KIPPING.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlviii., No. 6, February 8, 1909.

Role in Nature of the Dissociation of Carbonophosphates.—A. Barillé.—In a previous note the author has reported that carbon dioxide, in presence of water and under pressure, produces with phosphates the metals of which are capable of forming bicarbonates a new class of compounds, carbonophosphates, easily dissociated in air, which cannot be isolated from their solutions. In decomposing these carbonophosphates yield two substances, a dibasic phosphate and the corresponding bicarbonate, which finally becomes a neutral carbonate. Thus the dissociation of carbonophosphates explains many very different natural phenomena, e.g., the maintenance of the comparatively high tension of carbon dioxide in the blood, and the assimilation of phosphates by plants.

Coking of Coal.—O. Boudouard.—Various organic solvents such as ligroin, benzene, naphthalene, &c., have very little or no modifying action on the quality of coke given by coal, and by evaporation of the solvents tarry brown masses are obtained in small proportions, except in

the case of pyridine, which dissolves more than 10 per cent of them. Concentrated hydrochloric acid has no action. Concentrated nitric and sulphuric acids cause coals to lose their power of giving coke. Fused potash and Schweitzer's reagent both diminish it. The successive actions of aqueous potash, concentrated hydrochloric acid, and Schweitzer's reagent completely destroy it, apparently because the cupropotassic liquid dissolves all matter of cellulose origin. The humic acid found in non-coking coal is derived from these hydrocarbons existing in a more or less polymerised state in the coal. The fact that anthracites do not give agglomerated coke can be explained very readily. This variety of coal represents a very advanced state in the transformation of vegetable matter and does not contain cellulose, and humic matter cannot be detected in it.

Indigoid Colouring Matters derived from Phenylisoxazolone.—A. Wahl.—Products characterised by the

chromophone group $\begin{array}{c} -C = C- \\ | \quad | \\ -CO \quad CO \end{array}$ can be prepared by the

action of isatin chloride upon phenylisoxazolone and its derivatives. Methoxyphenylisoxazolones are thus converted into the corresponding indolindigos, which are coloured crystalline products. They give a violet coloration with soda or alcoholic ammonia, and the addition of sodium hydrosulphite to the alkaline solution gives a yellow liquid from which acids do not precipitate the colouring matter, which only reappears upon the addition of an oxidising agent such as hydrogen peroxide.

MEETINGS FOR THE WEEK.

MONDAY, 29th.—Royal Society of Arts, 8. (Cantor Lecture). "Steam Turbines," by G. Gerald Stoney.

TUESDAY, 30th.—Royal Institution, 3. "Evolution of the Brain as an Organ of Mind," by Prof. F. W. Mott, F.R.S.

WEDNESDAY, 31st.—Royal Society of Arts, 8. "The Island of St. Helena," by J. C. Melliss.

THURSDAY, April 1st.—Royal Institution, 3. "Aërial Flight in Theory and Practice," by Prof. G. H. Bryan, F.R.S. Chemical, 8.30. "Affinity Values of certain Alkaloids," by V. H. Veley. "Preparation and Properties of the *n*-Tribromo Substituted Hydrazines, usually styled the Diazo-perbromides," by F. D. Chattaway. "The Coloured Salts and Derivatives of the Thio-violic Acid Group," by P. C. C. Isherwood. "Nitrosoacetyl-amino-derivatives of the Benzene and Diphenyl Series," by J. C. Cain. "Observations on Phycoerythrin, the Pigment of the Red Algae," by E. K. Hanson.

FRIDAY, 2nd.—Royal Institution, 9. "Electrical Striations," by Prof. Sir J. J. Thomson, F.R.S.

SATURDAY, 3rd.—Royal Institution, 3. "Properties of Matter," by Prof. Sir J. J. Thomson, F.R.S.

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Mdme. CURIE'S Thesis

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THE CHEMICAL NEWS.

VOL XCIX., No. 2575.

ON THE REDUCING ACTION OF ELECTROLYTIC HYDROGEN ON ARSENIUS AND ARSENIC ACIDS WHEN LIBERATED FROM THE SURFACE OF DIFFERENT ELEMENTS.*

By WILLIAM THOMSON, F.I.C.

THIS research was commenced with a view to find the velocity at which arsenic was liberated as arseniuretted hydrogen from cathodes of different elements:—

- (a) From arsenic in the form of arsenious acid.
- (b) From arsenic in the form of arsenic acid.

The experiments were carried out in the apparatus already described by me (*Memoirs and Proceedings of the Manchester Literary and Philosophical Society*, xlviii., Part III., No. 17), which consists of a porous pot containing 30 cc. of dilute sulphuric acid (one of strong acid to six of water by volume), with the cathode, when that was possible, in the form of a cylinder 60 mm. long and 10 mm. diameter, immersed to a depth of 27 mm., giving a surface exposed to the electrolyte of 8.48 square centimetres, the end passing through an india-rubber cork fitted into an opening in the glass stopper, which was accurately ground into the mouth of the porous pot and made air-tight with vaseline; the liberated hydrogen was passed from a glass tube fused into the same glass stopper, which ended in a two-way tap and T-piece. Another similar apparatus was placed in series with the first-mentioned, so as to liberate hydrogen from pure dilute sulphuric acid. This apparatus was also provided with a two-way tap and T-piece, so that a stream of pure hydrogen, dried through a calcium chloride tube and passed over a small roll of dry basic lead acetate paper to remove any trace of H_2S , could be passed through one or other of two drawn-out hard glass tubes which were heated to redness near to the drawn-out ends to receive the arsenic mirrors. These were deposited on the drawn-out part, the diameter of which was graduated by inserting a wire, the one end being 1.6 mm., the other 1.1 mm. diameter, the length between these two points being 2 mm., the tube being cooled from the larger diameter. This apparatus was capable of easily detecting 0.000,000,5413 grm. (roughly about 1/2,000,000 of a grm. of elemental arsenic when contained in the 30 cc. of acid in the porous pot. This quantity was taken as a unit, and for each experiment 5 cc. of a solution containing 0.000,005,431 grm. per cc. was taken in the form of—

- (a) Arsenious acid.
- (b) Arsenic acid.

This makes 50 units, each of which can be easily detected. This amount was deduced from another standard in which 50 cc. of a liquid containing 1/1000th of a grain per gallon produces a well-defined mirror of arsenic on the cooled drawn-out part of the glass tube.

Having filled the apparatus with hydrogen by passing a current of 3 amperes through 10 cc. of dilute sulphuric acid in the porous pot, 5 cc. of the standard solution of arsenic above mentioned is made up to 15 cc. with dilute sulphuric acid, and poured into the apparatus by a funnel fused into the glass stopper of the porous pot, stoppered by a glass rod at the bottom, the funnel being rinsed into the porous

pot with 5 cc. of the same dilute acid. After the apparatus has worked for two and a-half minutes and a mirror has been deposited, the two-way tap is turned so that the hydrogen from the apparatus in series generating pure hydrogen sweeps the tube for a few moments. The tube is then removed, and another inserted to receive a fresh mirror, the second mirror being produced by the two-way tap diverting the flow of the hydrogen containing arseniuretted hydrogen for two and a-half minutes to the second tube, through which pure hydrogen had previously been passing, and which was heated to redness for the purpose of receiving the second mirror. In this way mirrors were received without loss of arsenic on the drawn-out portion of hard glass tubes, cooled at the point at which the mirror was to be deposited by means of cold water flowing continually over them. The mirrors thus received were sealed off in an atmosphere of dry hydrogen, and the quantity on each estimated by comparison with a series of standard mirrors examined and compared by a magnifying glass.

Plotting the amounts of arsenic deposited in successive intervals of two and a-half minutes as the ordinates, and the time as abscissæ, curves were obtained for all these experiments. It was observed that, however carefully each experiment was repeated, no two results agreed absolutely, and this disagreement was greater for arsenic acid than for arsenious acid.

Thirteen different elements were tested—viz., lead, zinc, cadmium, tin, silver, graphite, iron, platinum, aluminium, gold, cobalt, nickel, and palladium*—and the order given above is the order in which they are capable of removing arsenic from solution as arseniuretted hydrogen when it exists in solution in the form of arsenious acid. This order, however, does not hold for the relative power of the different elements for removing arsenic from solution as arseniuretted hydrogen when it exists as arsenic acid in the electrolyte.

Chapman and Law ("The Reducing Action of Hydrogen," Part II.; "The Estimation of Traces of Arsenic by the Marsh-Berzelius Method and the Insensitiveness of Zinc," *Analyst*, 1906, xxxi., 3) suggest that the reducing efficiency of hydrogen with respect to arsenious and arsenic oxides depends largely upon the supertension† of the cathode at which the hydrogen is liberated, and they put forward a formula to explain this as follows:—



"where A_s represents the amount of unreduced arsenious oxide and K a constant factor. If the equation be disturbed by the addition of A_s , i.e., if the factor A_s be increased, reduction takes place or the reaction proceeds from right to left, and the same result is reached if P_H is made larger. On the other hand, if P_H is made smaller, A_s must be made larger to preserve the equilibrium. In other words, there is always left in solution after each experiment a certain residuum of unreduced arsenious oxide."

MA_sH_3 is a minute quantity of arseniuretted hydrogen always left in solution, and P_H the potential of the hydrogen effecting the reduction. The results we have obtained contradict this hypothesis.

The following table shows the relative velocities of thirteen different elements in decomposing arsenious and

* The following metals were used in the form of cylinders:—Lead, zinc, cadmium, and tin. Iron was used in a cylindrical form made by wrapping pure iron wire on a cylinder of glass, giving about the same surface exposed to the electrolyte as the metallic cylinders. The graphite electrode was cut in the form of a rectangular block giving about the same surface as the cylinder, and all the others were used in the sheet form; but it was found that the area of the cathode did not materially affect the result.

† "Supertension" of an electrode, according to Caspari ("Ueber-spannung," *Zett. Physikal. Chem.*, 1899, xxx., 89) is the excess of electromotive force necessary for the liberation of hydrogen at that electrode over the electromotive force required for the reversible production of hydrogen on a cathode of platinised platinum. The values of the "excess-voltage" or supertension for different metals are given by Caspari in his paper, and also in Leffeldt's "Electrochemistry," Part I., p. 176.

arsenic acids respectively, and the supertension of each element is also given when obtainable.

The figures in Table I. represent units of arsenic as above described liberated in twenty-five minutes from 50 units (taken as 100 half-units) of elemental arsenic contained in the electrolyte (a) as arsenious acid, and (b) as arsenic acid.

It was found that the current density had little influence on the result. The metals which could be easily melted were formed into cylinders 1 cm. diameter, and immersed to the depth of 2.7 cm., giving a current density of $C_{100} = 35$ (i.e., the current density was at the rate of 35 amperes distributed over 100 square cm. of surface). When the cathode had to be used as a sheet, the current density was $C_{100} = 3.5$, the surface being ten times greater.

TABLE I.—Showing the Relative Amounts of Arsenic removed as Arseniuretted Hydrogen from (a) Arsenious Acid and (b) Arsenic Acid from 100 Parts introduced, in Twenty-five Minutes, when Working with Three Amperes.

Metal.	(a) Arsenious acid.	(b) Arsenic acid.	Supertension (volts).
Lead	100	98.5	0.64
Zinc	100	41	0.70
Cadmium ..	100	27	0.48
Tin	100	18.5	0.53
Silver	100	0	0.15
Graphite ..	100	4	—
Iron	93	40.5	0.08
Platinum ..	88.5	0	0.09
Aluminium ..	82	9	—
Gold	74	4	0.02
Cobalt	43.5	0	—
Nickel	42.5	0	0.21
Palladium ..	38	0	0.46

It will be seen that lead is the most efficient of the elements examined, and it is remarkable that it liberates arsenic as arseniuretted hydrogen (AsH_3) when it exists in solution as arsenic acid almost with the same velocity as when it exists as arsenious acid. Lead has a high supertension, but not so high as zinc; and whilst both of these metals liberate arsenic at about the same velocity from arsenious acid, lead liberates as AsH_3 98/100ths of the arsenic present as arsenic acid in twenty-five minutes, whilst zinc only liberates 41/100ths of the amount present in the same time.

The next remarkable metal in the series is silver, with a very low supertension of 0.15, as compared with lead 0.64 and zinc 0.70. It liberates arsenic as AsH_3 from arsenious acid with about the same velocity as lead or zinc, whilst it is powerless to liberate any arsenic when it exists in the form of arsenic acid under the conditions of the experiment.

Again, palladium, which has a comparatively high supertension, is at the bottom of the series as regards efficiency in decomposing either arsenious or arsenic acid. Gold, which is at the bottom of the series as regards supertension, has the power of decomposing arsenious acid to the extent of three-quarters of the most efficient elements, and it does decompose some arsenic acid, whilst palladium is powerless to decompose any.

Iron, in this respect, is a remarkable metal, with the lowest but one supertension; it decomposes arsenious acid nearly as rapidly as lead, and it stands second (next to lead) in its power of decomposing arsenic acid.

These experiments show, I think, that the power of any element to decompose arsenious and arsenic acid is a peculiarity of the individual metal, and appears to be independent of its supertension.

If we take the first five elements (Table II.), it will be seen that the average velocities with which they decomposed arsenious acid into arseniuretted hydrogen are:—

TABLE II.—“Units” of Arsenic evolved as AsH_3 from 50 Units taken.

Intervals in minutes.	Lead.	Zinc.	Cadmium.	Tin.	Silver.
2½	9	8.5	8.5	9	6
5	13	14.5	12.5	12.5	12
7½	8.5	7.5	8.5	8	10.7
10	7	6	6.5	6.5	7.3
12½	5.5	4	5	4.25	5
15	4	3	3.5	3.5	3.8
17½	2.25	2.5	2.5	2.75	2.7
20	1.5	1.75	2.25	2	1.3
22½	1	2	1.5	1.75	0.8
25	0.5	1	1.25	1.25	0.3
Totals ..	52.25	50.75	52.0	51.5	49.9

It will be seen that the first figure is always lower than the others; this was due to residual hydrogen in the apparatus, although it was made as small as possible, the total volume being 20 cc. of air-space in tubes and apparatus with 30 cc. of electrolyte (3 amperes liberates 21 cc. per minute).

These results are averages of two or more experiments. Allowing for experimental error, a constant is obtained for these first five metals for a unimolecular velocity reaction, and this is one of the few electro-chemical reactions in which such velocities can be measured.

If a is the original concentration of the arsenious acid, and x the quantity transformed at the time t , the rate of transformation at that time will be, according to the unimolecular formulæ—

$$\frac{dx}{dt} = k(a - x),$$

where dx represents the very small quantity transformed in the very small interval dt starting at the beginning of the time t , and k is the coefficient of the velocity of the action. From this equation the integral calculus enables us to find a relation between x and t , the corresponding values for any stage of the reaction, in terms of the original concentration and the velocity constant.

This relation has the form—

$$\frac{t}{a} \log \frac{a}{a-x} = k.$$

On calculating x for the different two and a-half minutes intervals when using the mean constant k (obtained from the experiments), the calculated curve falls a little more rapidly at first than the curve obtained from the mean of the experimental results for the first four elements taken as cathodes, but after twelve minutes it crosses the line of the experimental curve and continues a little above it, up to the end, viz., twenty-two and a-half minutes; the two curves, however, are so close together throughout as to show that the reaction with the first four elements is unimolecular.

It was observed that if the amount of arsenic in the form of arsenic acid were increased in the cathode chamber, one arrived at a point when the cathode elements, which liberated no arseniuretted hydrogen under the ordinary conditions of the experiment, were capable of giving a small mirror on working the apparatus continually for forty-five minutes, and Table III. shows the results:—

TABLE III.—Elemental Arsenic in the Form of Arsenic Acid in 30 cc. expressed in—

	Units as above described.	Millionths of a gram.
Nickel	20	10.8
Platinum	90	48.7
Silver	140	75.8
Palladium	191	103.5

An attempt was made to measure the velocity of the reduction when using a copper cathode with As_2O_6 . No arseniuretted hydrogen was given off until the copper had

become covered with a brownish black deposit which gave by two analyses of small quantities the formula Cu_3As .

Chapman and Law found the same deposit, which they regarded as one of elemental arsenic. On making other experiments we obtained no deposit on the copper and no arseniuretted hydrogen evolved.

With an electrolyte composed of 5 per cent sodium hydrate solution we did get arseniuretted hydrogen evolved as follows:—

Minutes $2\frac{1}{2}$ 5 $7\frac{1}{2}$ 10 $12\frac{1}{2}$ 15 $16\frac{1}{2}$
Units obtained from
50 units added . . . 0 2 3.5 2.5 2.5 1.5 1 = 13

We tried the element magnesium as a cathode in a similar way to the other metals, but found it dissolved rapidly in the electrolyte whilst the current was passing.

I have to acknowledge the services of my assistant, Mr. L. L. Bircumshaw, for the perseverance and industry which he has exercised continuously during the last fourteen months in carrying out this investigation with me.

IMPROVEMENTS IN PRODUCTION AND APPLICATION OF GUNCOTTON AND NITROGLYCERIN.*

By Colonel Sir FREDERIC L. NATHAN, R.A.

(Concluded from p. 153).

NITROGLYCERIN powders are cheaper than nitrocellulose powders weight for weight, and even more so for equal ballistic effects.

The original cordite, the manufacture of which commenced in 1890, contained a high proportion of nitroglycerin, 58 per cent, and the erosion produced, especially in large guns, was considerable. This led to experiments being carried out at Waltham Abbey, with a view to the production of a less erosive explosive, and the final result was the introduction into the service, in 1901, of a modified cordite known as "cordite M.D.," in which the percentage of nitroglycerin is reduced to 30 per cent, so that the composition becomes nitroglycerin, 30 per cent; guncotton, 65 per cent; and mineral jelly, 5 per cent.

The constants of explosions of cordite, and cordite M.D., determined at the Royal Gunpowder Factory, some little time ago, are as follows:—

	Cordite.	Cordite M.D.
Density of loading	0.2	0.2
Heat of explosion at constant volume, water gaseous (calories per grm.) . .	1156	965
Total gases, water gaseous, at 0°C ., 760 mm. (cc. per grm.)	871	920
Temperature of explosion ($^\circ\text{C}$.) . . .	2663	2374

An inspection of these figures shows that the alteration in proportions of the explosive ingredients results in a decrease in the heat of explosion of about $16\frac{1}{2}$ per cent, and an increase in the volume of gases of about $5\frac{1}{2}$ per cent, whilst there is a decrease of 289°C ., in the temperature of explosion.

As would therefore be expected the erosion produced by cordite M.D., is very much less than that produced by the original cordite for the same ballistics, and is certainly not greater, if as great, as that produced by the best forms of nitrocellulose explosives.

Although of minor importance to smokelessness, flamelessness is a desirable quality for propulsive explosives to possess. In this respect cordite M.D. is superior to cordite in the case of rifles and machine guns; unfortunately, a suitable ingredient has not yet been discovered which will render smokeless powders flameless in large guns.

A third ingredient in both natures of cordite, viz., mineral jelly, although present in a comparatively small proportion, is a very important constituent.

Cordite in the advanced experimental stage consisted of nitroglycerin and guncotton alone, and as their combustion produced no solid residue of any kind, the surface of the bore of the magazine rifle in which the early experiments took place was not fouled in any way. The result was that the cupro-nickel coated bullets, propelled in succession at high velocity through a clean barrel, deposited some of the cupro-nickel in the bore. In order to prevent this a number of substances were incorporated with the nitroglycerin and guncotton, with the object of producing a deposit in the bore, which it was hoped would get rid of the difficulty of metallic fouling. Of all these various substances the one which appeared to answer the purpose most satisfactorily was refined vaseline, and this material became the third ingredient of cordite as eventually introduced into the British Service. When the manufacture was commenced on a large scale, vaseline, which is the proprietary name of one of the refined products of the distillation of petroleum, was replaced by mineral jelly, the same material, but in a cruder form.

The original object with which mineral jelly was introduced was of no importance when cordite was substituted for the black and brown powders used in large guns, but in order to have but one nature of smokeless powder in the service, mineral jelly was added to all cordite whether for use in small arms or artillery. Subsequent experience has demonstrated how very fortunate was the selection of this material for rifle cordite and the extension of its use to all sizes of cordite.

Mineral jelly is one of the best ingredients it is possible to have in smokeless powders from the point of view of their chemical stability. This important fact, not recognised originally, was brought out in the following way:—In order to facilitate the explosion of cordite in blank ammunition for the rifle, it was cut into very thin flakes, and the non-explosive mineral jelly was omitted from its composition. After a comparatively short storage in a hot climate, the stability of the smokeless blank, as it was called, was found to have suffered seriously, whereas the stability of normal cordite containing mineral jelly was not appreciably affected. These facts led to a thorough investigation at Waltham Abbey of the action of mineral jelly in preserving the stability of cordite, and it was discovered that mineral jelly contained constituents which had the valuable property of combining with the decomposition products (the result of prolonged storage of cordite at high temperatures) to form stable bodies, thus removing these decomposition products, which undoubtedly exert a deteriorating influence on the cordite, from their sphere of action.

When Abel was engaged on his researches in connection with the production and properties of guncotton, it was obvious to him that some test of a chemical nature was required, in order to ascertain whether or not the finished guncotton had been thoroughly purified in manufacture. It will be remembered that accidents occurred in the early days of its production because this purification had not been carried sufficiently far. The test which he devised was based on the principle that if guncotton be subjected to an elevated temperature, traces of oxides of nitrogen will be given off, and will reveal their presence by acting on a suitable reagent.

The test is carried out by heating guncotton in a test-tube placed in a water-bath, and suspending over it a strip of moistened filter-paper impregnated with potassium iodide and starch. If the purification of the guncotton has not been sufficient, the discoloration of the test-paper takes place early; as the result of experience Abel fixed a time before which no reaction should take place. This test, known as the Abel heat test, is a test for the purity of guncotton, and of nitroglycerin, and of freshly made explosives containing either one or both of these ingredients. For this purpose no test has yet been devised which equals it. But it was never intended to be, and is not, a quantitative test, and is therefore only a rough guide, though a very useful one, as to the stability of an explosive which

* A Discourse delivered before the Royal Institution, January 29, 1909.

has been in store for more or less prolonged periods, or under more or less adverse conditions.

Smokeless powders of the types dealt with are all subject to deterioration, and there is very little doubt that this deterioration is for any given explosive a function of the temperature of storage. The higher the temperature, the more rapid the deterioration.

The necessity therefore of some quantitative test which would enable a judgment to be formed as to the extent of deterioration suffered by any given sample of cordite is obviously of great importance, because such a test would afford the means of determining how much longer it would be safe to store any given batch of cartridges or lot of cordite at any given temperature. Any such test must be a heating test, and it must be possible to co-relate the temperature and duration of the test with any given temperature and duration of storage. The rate of deterioration as a function of the temperature was determined by Dr. Will for guncotton, and later by Dr. Robertson at Waltham Abbey for nitroglycerin. From these and other experiments carried out at Waltham Abbey, a factor of increase in rate of deterioration of cordite with increase of temperature was deduced. This factor having been determined, what is known as the "silvered vessel test" was worked out at the Royal Gunpowder Factory. In this test, of which the details will be described presently, cordite is heated in a specially designed vessel at 80° C., a temperature not too far removed from those to be met with when cordite is stored under the worst service conditions, and the number of hours heating at this temperature any given sample will stand before it shows signs of active decomposition are ascertained. Then, by means of an equation, containing the factor connecting rate of increase of deterioration with rise in temperature, a calculation can be made converting the hours of heating at 80° C. the sample withstood, to years and fractions of a year it would stand at any given temperature of storage, and therefore a knowledge is obtained of how much longer it would be safe to store this cordite at any given temperature.

This test was applied to a considerable number of samples of known age and thermal history. From these data and knowing the number of hours at 80° C. that newly made cordite of good stability will stand before showing signs of decomposition, the number of hours that the different samples should stand the test were calculated. When the samples were actually tested, the number of hours heating at 80° C. they withstood, were in close agreement with the number of hours it was calculated they should stand.

The form of vessel in which the heating is carried out is the well-known vacuum vessel of Sir James Dewar. A glass bulb silvered externally is enclosed in an outer bulb, silvered internally. The space between the two is highly evacuated for the purpose of limiting the dissipation of any heat evolved by exothermic changes on the one hand, and on the other for the purpose of minimising the effect of accidental slight changes in temperature of environment.

In the centre of the inner bulb is situated the bulb of a thermometer, the stem of which passes through a cork in the neck of the vessel. A side tube is attached for the purpose of making observations on the colour of the gases evolved. For heating the vessel a bath is provided with cylinders closed at the bottom, and wide enough to admit the vessel to such a depth as the side tube will permit. The bath is surrounded by insulating materials. The vessels are packed in the cylinders with wool yarn, and the tops of the cylinders are closed with felt discs, to exclude draughts.

The bath is fitted with a gas regulator or other means for securing that the temperature of the explosive is kept constant.

The cordite is coarsely ground, and 50 grms. are used.

Readings of the thermometer are taken at intervals, and the time is noted when a rise of 2° C. in the temperature of the explosive above the temperature of 80° C. occurs. At the same time, visual observations are made as to the colour of the column of gas in the side tube, since it is

found that previous to the rise in temperature occurring orange-coloured fumes of nitric peroxide are evolved. When the temperature exceeds 82° C., the test is complete and the flask is withdrawn. The number of hours which have elapsed since the start of the test is the measure of the stability of the cordite.

Until about sixty years ago the only explosive known, for all purposes, was gunpowder. With the discovery of guncotton and nitroglycerin, gunpowder was gradually replaced by them for blasting purposes. In their early days the two explosives were used singly, guncotton as guncotton, nitroglycerin—first of all alone—and then as dynamite. Later on, the two were combined as blasting gelatin, and explosives of a similar nature, but it was quite forty years after their discovery before either became of practical use for propulsive purposes.

The invention of "Poudre B" by Vieille marked the commencement of a new era in connection with the science of artillery, and it was not long before smokeless powders made from the violent guncotton or of guncotton combined with the still more violent nitroglycerin, entirely superseded the centuries-old gunpowder. Modern explosives are characterised by very greatly increased power, giving enormously greater range to projectiles fired from both rifles and artillery, thus altering entirely the condition of both land and naval warfare.

It is at present not easy to forecast in what direction further improvements in propellants will take place. It is also difficult to conceive what the explosive of the future will be which shall produce a change as revolutionary as that which took place when smokeless powders superseded the old-fashioned black powders. For some time to come, probably, the manufacturer of explosives will have to content himself with endeavours to improve them as far as he can both from a ballistic and from a stability point of view, with the ingredients now at his disposal.

THE ACTION OF CARBON DIOXIDE UPON NITRITES IN SOLUTION.

By ERNEST ROBERT MARLE.

THE action of carbon dioxide upon nitrites in solution has been studied recently by Moody, by Moore, by Marie and Marquis, and by Meunier.

Moody (*Proc. Chem. Soc.*, 1903, xix., 240) states that salts of weak acids, such as potassium and sodium nitrites, sodium formate, &c., are decomposed by carbon dioxide. Passing a slow stream of the gas for nine days through a solution containing 10 grms. of sodium nitrite, 1.585 grms. of sodium carbonate were obtained. A well crystallised specimen of sodium nitrite, free from carbonate, was used. Müntz (*Comptes Rendus*, 1891, cxii., 1142) found that calcium nitrite, in sterilised soil, gave nitrogen peroxide rapidly in the presence of carbon dioxide. Marie and Marquis (*Comptes Rendus*, 1904, cxxxviii., 367) find that pure carbon dioxide liberates iodine from potassium iodide in the presence of sodium nitrite, and that a solution of potassium iodide containing starch is coloured blue by carbon dioxide which has passed through a solution of sodium nitrite. Moore (*Journ. Am. Chem. Soc.*, 1904, xxvi., 959) also concludes that that nitrous acid is expelled by carbon dioxide.

Meunier (*Comptes Rendus*, 1903, cxxxvii., 1264) claims that the presence of nitrous acid or anhydride under these circumstances is due to the presence of the potassium iodide or of other halogen salts.

The uncertainty upon this point seems to be due partly to the use of potassium iodide and starch as a test for nitrous acid. Thus, Papasogli (*Gazzetta*, 1881, xi., 277) finds that carbon dioxide at low temperatures, while it does not decompose pure potassium iodide, in the presence of a trace of iodate, causes the liberation of iodine. Potassium hydrogen carbonate slackens, and may prevent the action of the gas upon the mixture. Pellagri (*Gazzetta*, vii., 297) states that carbon dioxide liberates hydrogen

iodide from solutions of potassium iodide, and, if iodate be present, iodine is set free even in the absence of light.

The present author found that potassium hydroxide (which gave no indication of nitrite with α -naphthylamine), when neutralised with hydrochloric or sulphuric acid, gave a distinct coloration with potassium iodide and starch. The colour was faint, but more pronounced than that produced by hydrochloric acid alone. Potassium iodide was mixed with potassium hydroxide solution, and the mixture was allowed to stand some time in the cold; it was then neutralised, and starch was added; a faint colour appeared almost at once. If the solution was boiled for a minute before neutralising, starch gave an immediate blue colour. In all cases a considerable precipitate formed on standing for some hours.

Hence the coloration of a solution of potassium iodide and starch cannot be regarded as conclusive evidence of the presence or absence of free nitrous acid, particularly if the latter be present only in minute quantity.

The author found that, in the following experiments, a solution of potassium iodide and starch was coloured by the solutions in question to a slightly greater degree than by the reagents alone.

The carbon dioxide used was prepared from marble by the action of hydrochloric acid in Kipp's apparatus, and was washed by passing through two Drechsel bottles containing water. The water in the second bottle gave no milkiness with silver nitrate after passing the gas for nine hours.

The gas was next passed through potassium nitrite solution (about 10 per cent) contained in a Clœz washing-bottle, the construction of which renders it unlikely that any of the liquid will be mechanically carried over by a current of gas. After passing through the nitrite solution, the gas was led either into water or into a strong solution of potassium or sodium hydroxide.

The liquid in the final flask in all cases gave a coloration with α -naphthylamine, and the presence of potassium hydroxide seemed to make little or no difference to the result. After passing the gas for from one to four hours, the colour began to appear in from five to fifteen minutes; after six and a-half hours a faint colour appeared in three minutes. When the nitrite solution was heated to about 80°C ., the action seemed to take place more rapidly.

To guard against the possibility of mistaking potassium nitrite, mechanically carried over by the stream of gas, for nitrous acid, a well-dried Arnold absorption apparatus was inserted between the Clœz bottle containing the potassium nitrite and the water used for collecting any nitrous acid that might be formed. Carbon dioxide was passed for two hours; a slight mist appeared on the inside walls of the absorption bulbs, which, being washed out with distilled water, gave a faint acid reaction, and produced with α -naphthylamine a deep red colour which began to appear in about half a minute. The water through which the gas was bubbled was neutral to litmus (after boiling), and gave a very faint pink colour with α -naphthylamine, appearing in about fifteen minutes and remaining faint.

In a subsequent paper it will be shown that potassium dichromate expels nitrous acid in dilute solutions of nitrites, without the formation of oxides of nitrogen. A solution of potassium nitrite containing more than half its molecular equivalent of potassium dichromate has an acid reaction, and may contain free nitrous acid. Carbon dioxide was found to remove nitrous acid from such a solution to a slightly greater extent than from the nitrite alone.

It seems certain from these experiments that carbon dioxide breaks up potassium nitrite, and that the gas can carry away traces of nitrous acid from the solution. From the data in Warington's paper (CHEMICAL NEWS, 1885, li., 39), the quantity of nitrogen, as nitrous acid, removed by 1 litre of carbon dioxide is probably less than 0.005 mgrm. The reduction of dilute permanganate solution leads to a similar figure.

THE RELATION BETWEEN COMPOSITION AND CONDUCTIVITY IN SOLUTIONS OF META- AND ORTHO-PHOSPHORIC ACIDS.*

By E. B. R. PRIDEAUX, M.A., D.Sc.

EVER since Graham's classical researches on the phosphoric acids, the changes which they undergo in aqueous solution have been a subject of discussion among chemists. The principal instruments of investigation have been:—(1) Qualitative tests which distinguish HPO_3 , $\text{H}_4\text{P}_2\text{O}_7$, and H_3PO_4 from one another more or less sharply; (2) quantitative tests, more especially the different behaviour of the three acids with indicators; (3) thermochemical data.

Up to the present the electrical conductivity has been scarcely used as a measure of the mutual changes of these acids, and it was with the object of correlating electrical conductivity with compositions of aqueous solution as deduced by method (2) that the following research was undertaken. The result has been to establish for acid of a particular concentration relations between conductivity, composition, and time.

The proof, due to Graham, that there are three distinct degrees of basicity corresponding to degrees of hydration of P_2O_5 at once raised the question, Which of these was present in solutions prepared by adding P_2O_5 or HPO_3 to water? It was known that the final product was in all cases H_3PO_4 , and Graham himself held that HPO_3 was transformed into H_3PO_4 ; Berzelius, on the other hand, held that $\text{H}_4\text{P}_2\text{O}_7$ was first formed and then by further hydration converted into H_3PO_4 .

Succeeding investigators have held the one or the other hypothesis, but a survey of their work shows a preponderating balance in favour of the view that $\text{H}_4\text{P}_2\text{O}_7$ is not formed in any notable quantities when P_2O_5 or HPO_3 are dissolved in water.

Sabatier (*Ann. Chim. Phys.*, 1899, [6], xviii., 409), whose paper is the most complete study of the change of HPO_3 into H_3PO_4 , considers that $\text{H}_4\text{P}_2\text{O}_7$ may be formed to a slight extent when solid HPO_3 is first added to water, but is not produced at all by any subsequent transformation of dissolved HPO_3 . Péligot (*Ann. Chim.*, 1840, lxxiii., 286) stated that syrupy H_3PO_4 when kept for a long time deposited two kinds of crystals, of which one kind lost about 23 per cent of water when heated with PbO and was $\text{H}_4\text{P}_2\text{O}_7$.

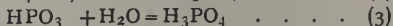
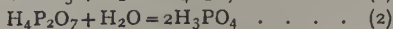
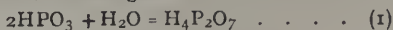
Thomsen thought he detected $\text{H}_4\text{P}_2\text{O}_7$ in aqueous solutions, prepared as above, from a consideration of heats of neutralisation. But Sabatier remarks that the heats of neutralisation of the second and third H atoms are small and do not furnish very certain evidence. Girau (*Comptes Rendus*, vol. 134, 135, 136) also studied the question from the thermochemical point of view. He mentions that the heat of neutralisation of HPO_3 is that of a strong monobasic acid, while those of H_3PO_4 and $\text{H}_4\text{P}_2\text{O}_7$ are considerably less. From this evidence, along with the heat of solution, he concludes that fresh solutions of HPO_3 change into $\text{H}_4\text{P}_2\text{O}_7$ and H_3PO_4 , and that the first change takes place quickly and the second slowly. This is not easy to reconcile with the work of Berthelot (*Comptes Rendus*, 1896, cxxiii., 776) and Sabatier (*loc. cit.*). The former finds that a solution of $\text{H}_4\text{P}_2\text{O}_7$ containing the equivalent of 15.6 grms. of P_2O_5 to the litre is half transformed into H_3PO_4 at room temperature in 121 days, while the latter finds that acid of the same P_2O_5 content, present as HPO_3 , is under similar conditions half transformed in thirty days.

The effect upon indicators of the different H ions of HPO_3 , $\text{H}_4\text{P}_2\text{O}_7$, and H_3PO_4 is as follows:—

The first H ion of all three acids is acid to methyl orange, the second both of $\text{H}_4\text{P}_2\text{O}_7$ and H_3PO_4 to phenolphthalein.

* A Paper read before the Faraday Society, March 30, 1909.

Considering, then, the changes—



Change (1) would be associated with a decrease in the methyl-orange titre. Berthelot (*loc. cit.*) has studied change (2), and shown that the acid titre to methyl-orange increases, while that to phenolphthalein remains the same. But in the solutions prepared by adding P_2O_5 or HPO_3 to water, invariably the titre to methyl-orange remains constant, and that to phenolphthalein increases corresponding to change (3), or to a slow change (1), followed by a rapid change (3). In the latter case, however, there would only be at each moment a very small proportion of $\text{H}_4\text{P}_2\text{O}_7$ present in the solution, and this could be left out of account for the purposes of the present investigation. Further, the solution was tested for $\text{H}_4\text{P}_2\text{O}_7$ at several stages, both by adding zinc acetate and acetic acid, and also by adding silver nitrate and excess of acetic acid to the solution of sodium salt. The pyrophosphate in each case would remain undissolved. In each case a clear solution was obtained; pyrophosphate was therefore absent.

With regard, then, to the change of HPO_3 into H_3PO_4 the following facts were established by Sabatier. His

of transformation, that HPO_3 is a condensed acid, and the process one of depolymerisation.

It is known that fused HPO_3 is polymerised and also HPO_3 in acetic acid solution (*Comptes Rendus*, June 29, 1908), and it may quite probably also be polymerised in aqueous solution, yet an investigation of the above formula rather tends to show that, considering these results only, the process is mainly one of hydration. For although in any one such solution the reaction behaves as if it were unimolecular, that is by no means a proof that the process is really unimolecular, and to be represented by some such equation as $(\text{HPO}_3)_n = n\text{HPO}_3$.

Bearing in mind that the solutions had never a total concentration more than double normal, it is evident that the concentration of the water, being of another order from that of the HPO_3 , will practically remain constant throughout, and the reaction $\text{HPO}_3 + \text{H}_2\text{O} = \text{H}_3\text{PO}_4$ therefore behaves as unimolecular.

Further, the value of $\log a$ was found to vary on passing to a solution of different total concentration, and this again points to the probability that the reaction is really bimolecular and consists of a hydration of HPO_3 molecules.

The present work has revealed certain differences between the rate of transformation of HPO_3 solutions prepared as above and those prepared by adding P_2O_5 to water. The solution was quickly prepared by adding pure

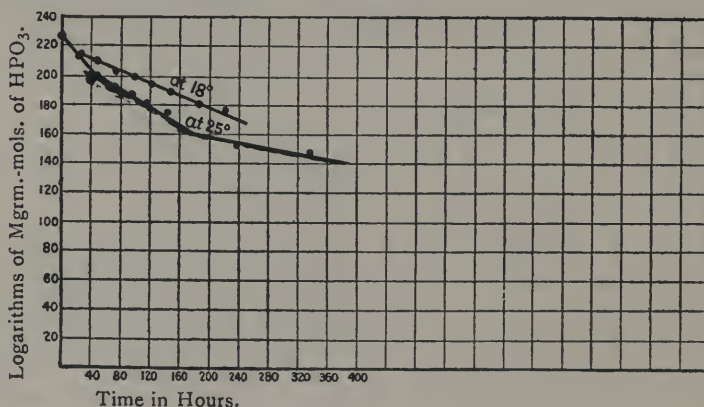


FIG. 1.—CHANGE OF HPO_3 AND TIME.

solution was usually prepared from H_3PO_4 which had been dehydrated at a red heat. He remarks that when P_2O_5 is dissolved in cold water, a solution is obtained which undergoes practically the same transformations as that prepared as above. That is to say, the HPO_3 present transforms itself into H_3PO_4 according to an exponential law with the time, the speed of transformation being at each instant proportional to the active mass of HPO_3 . If this concentration expressed in mgrm. molecules per litre is denoted by Γ_{HPO_3} and time by t , then log—

$$\Gamma_{\text{HPO}_3} = -t \log a + \log b \quad \dots \quad (1),$$

where a is a function of the temperature T and of the total concentration—

$$\log a = \lambda \mu^T \quad \dots \quad (2),$$

μ is constant and $= 1.125$ for all concentrations below $\Gamma = 1200$, while λ depends upon the concentration in such a way that—

$$\lambda = a \Gamma + \beta \quad \dots \quad (3),$$

Combining (3) and (1) and putting in the values for the constants a , β , and μ —

$$\log a = \mu^T (a \Gamma + \beta) \quad \dots \quad (4)$$

$$\log a = 1.125 (0.06 \Gamma + 0.0322) \quad \dots \quad (5)$$

The author concludes, from the fact that decrease of concentration of HPO_3 is associated with a smaller velocity

P_2O_5 to water at room temperature. By this means a solution is obtained which does not contain so high a percentage of HPO_3 as that from glassy HPO_3 and water at 0° , but it contained sufficient for the present purpose. It is hoped to investigate at some future date solutions containing over 90 per cent of HPO_3 .

Under the conditions mentioned above a fairly constant percentage of HPO_3 is obtained, as may be seen from the following figures :—

Total acid. Equivalents per litre.	Mgrms. per litre.	Per cent HPO_3 in total acid.
244		78.9
237		74.0
235		74.4
240		75.4
254		30.10

(a) P_2O_5 thrown quickly into water.

(b) P_2O_5 allowed previously to deliquesce.

The solution became clear in about half an hour, and was then placed in the thermostat at 18° or 25° . It was kept in bottles furnished with glass or rubber stoppers. Samples were taken out from day to day, placed in test-tubes, and the conductivities measured with a dip electrode, the capacity of which had been fixed by $\text{N}/10\text{KCl}$. The sample was then immediately titrated in the presence

first of methyl-orange and then of phenolphthalein, and the amounts of HPO_3 and H_3PO_4 deduced as above. The constancy of the methyl-orange titre gave a sufficient guarantee that no evaporation had taken place. The electrically heated and controlled thermostats have been described by Dr. Gibson (*Proc. Roy. Soc. Edin.*, June 22, 1908).

During the time of conductivity experiments, which lasted for about fourteen days, the 25° thermostat did not vary by more than 0.1° , and the 18° not more than 0.02° .

Two preliminary series of experiments were made to ascertain the nature of the change, and followed by two further series, which furnish the results summarised as follows:—

The total concentration was in both cases 0.240 of an equivalent total acid in the litre. In these figures

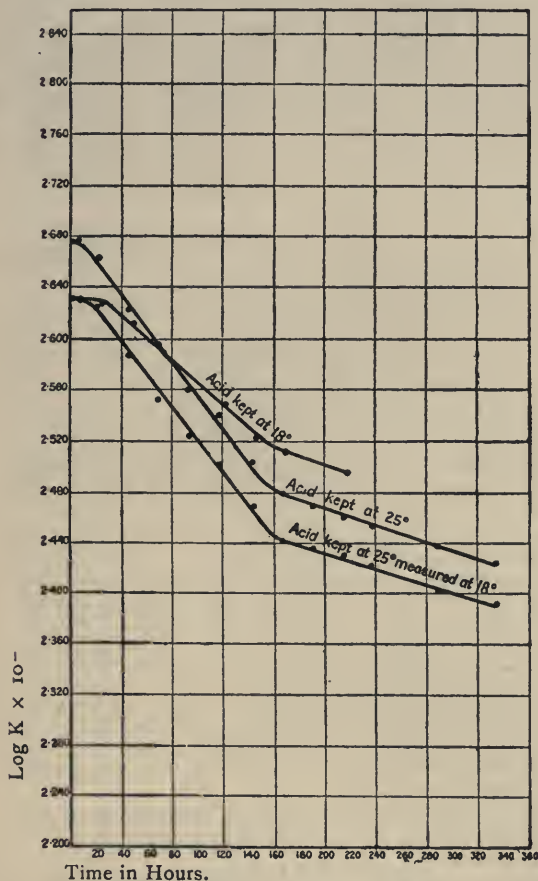


FIG. 2.—CONDUCTIVITY AND TIME.

ΓHPO_3 = concentration of HPO_3 expressed as mgrm molecules to the litre, K = specific conductivity $\times 10^4$, t = time in hours, T = temperature.

In Fig. 1 the lower line represents the change in $\log \Gamma$ plotted against time at 25° , the upper line the corresponding relation at 18° . If the rate of decrease were proportional to the amount of HPO_3 left in the solution, the line should be straight and uniformly inclined to the axis of abscissae. It is evident that this is not the case.

If the rate of change is expressed by the equation $\log \Gamma\text{HPO}_3 = -TA + \log B$, in which B is a constant and equal to the initial concentration of HPO_3 , and A is the $\log a$ of equation (5) above, A , instead of remaining constant throughout, changes to a new value twice during the time of experiment.

The numerical values are—

Γ .	A .
$181 - 100$	0.0057
$100 - 42$	0.0031
$42 - 29$	0.00096

A calculated from formula (5) above ($\Gamma = 240$ and $T = 25$) is 0.0069 . The corresponding values for 18° are—

Γ .	A .
$137 - 75$	0.0022
$75 - 58$	0.0016

while A calculated from formula (5) ($\Gamma = 240$, $T = 18$) is 0.0030 .

Conductivity and Time.

In Fig. 2 $\log K$ is plotted against time. For the first twenty hours there is only a slight change in the con-

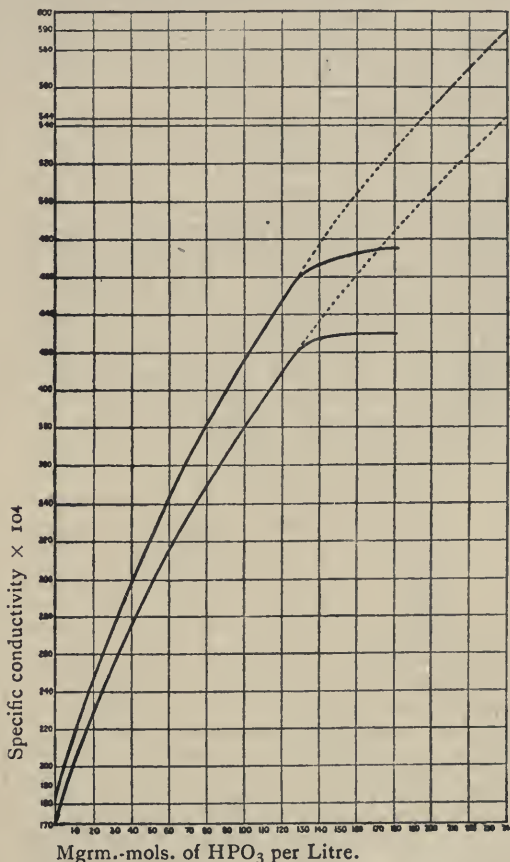


FIG. 3.—CONDUCTIVITY AND AMOUNT OF HPO_3 .

ductivity, after that the rate of decrease becomes more rapid, and follows an exponential law till about 160 hours after the commencement, when the straight line alters its direction, the rate of decrease becoming slower. This alteration of direction takes place at about the same concentration at which the rate of decrease of ΓHPO_3 begins to grow markedly less.

The $\log K$ and t graph resembles then, on the whole, that $\log \Gamma$ and t , except that the former shows a period of induction which does not appear in the latter. Excluding, then, this first part, the alteration in change of HPO_3 is associated with a similar alteration in change of K .

In Fig. 3, $K \times 10^4$ are plotted against ΓHPO_3 , the upper curve being for 25° and the lower for 18° . When the

change is complete the conductivities should be those of H_3PO_4 at 25° and 18° . This was verified by boiling some of the acid in a sealed tube for several hours, then determining K_{25} and K_{18} and titrating. The value of K_{25} for H_3PO_4 of 0.24 equivalent per litre is found by interpolation of Kohlrausch's values for 0.125 and 0.250 concentration to be 188. The value found as above is 186, and that for K_{18} is 173.

Temperature Coefficient of Conductivity.

From Fig. 3 the differences between the conductivities at 25° and 18° of acids having the same composition is seen to vary from about 45 units when HPO_3 is present to the extent of 181 mgrm. molecules down to 13 units when there is no HPO_3 . The percentage increase of conductivity between 18° and 25° does not vary much, being on an average about 1.2.

The point ΓHPO_3 and K in Fig. 3 lie approximately on a circular arc of large radius—90 per cent of them being within 2 units of abscissæ from the curve. The observed irregularities are, no doubt, due to the want of sharpness in the end-point when the second hydrogen ion of H_3PO_4 is estimated by its action on phenolphthalein. When a concentration of 181 mgrm. molecules of HPO_3 is reached, however, the points leave these curves and turn sharply to the right. The meaning of this is that at the beginning of the reaction, whilst the total concentration of HPO_3 is changing rapidly, the conductivity is increasing only slightly. Nothing certain can be said as to the theoretical conductivity of a mixture of HPO_3 and H_3PO_4 in varying proportions and the same total concentration, since the conductivity of pure HPO_3 and its dilution constant are unknown. But the above curve shows that the conductivity is a continuous function of the concentration of HPO_3 in the mixture, provided the observations are begun about twenty hours after the solution of the P_2O_5 . During this first period the conductivity is highly irregular, varying from one solution to another of the same composition by titration; but after this time solutions of the same composition had the same conductivities. There is a strong probability that this relatively slight increase of conductivity in fresh solutions is due to the presence of much polymerised HPO_3 , and this probability is strengthened by evidence drawn from the refractivity. J. S. Blake (*Am. Chem. Journ.*, xxvii., p. 72) has observed that the refraction of a solution of HPO_3 is different from that of H_3PO_4 at the same concentration. A spot of light traversing the changing solution was allowed to make its trace upon vertically moving paper, and the horizontal distances of this trace from a zero vertical straight line were taken as ordinates proportional to the amount of unchanged HPO_3 in the solution. It was found, however, that on mixing together fresh and old solutions in such proportions as should, by their concentration in HPO_3 , give an ordinate equal to 50 per cent of the highest ordinate of the self-changing solution, the ordinate actually obtained was only 40 per cent, or four-fifths of that expected. In other words, there is something present in the freshly prepared solution which has a greater retarding effect upon light than the half-altered HPO_3 . This is doubtless polymerised HPO_3 . An experiment was undertaken on these lines, substituting conductivity for refractivity. The conductivities and concentrations of a freshly prepared and an old solution having the same total equivalents per litre were separately measured, the conductivities being 458 and 230. These two acids were mixed in equal proportions, and the concentration of HPO_3 in the mixture was, of course, found to be the mean of the two concentrations. The conductivity of the mixture was 335, not far from the mean conductivity 344. But, as seen from Fig. 3, K_{18} for a self-changed acid of the same concentration is 393. This is again evidence that in the solution made up with fresh acid there is a much larger proportion of badly conducting acid than in that which has been allowed to change of itself to the same HPO_3 concentration. It seems probable that the lower part of the curve in Fig. 3 represents the

relation between conductivities and concentrations of simple molecules HPO_3 and H_3PO_4 . If the curve is continued on this assumption, the point where it strikes the ordinate from $\Gamma\text{HPO}_3 = 240$ represents the theoretical conductivity of HPO_3 . The conductivity so found is 544 at 18° and 590 at 25° , the per cent increase for 1° being 1.2, as in solutions of partly changed HPO_3 . If this does represent the conductivity of unpolymerised HPO_3 , it is interesting to notice that it is of the same order as that of HIO_3 at $1^\circ = 250$, namely, 573.

Summary.

When P_2O_5 is thrown into excess of water at room temperature, about 75 per cent of the total dissolved acid is HPO_3 and the rest H_3PO_4 . There is no evidence of the formation of $\text{H}_4\text{P}_2\text{O}_7$. This HPO_3 exists as complex and simple molecules, and the proportions of the two may vary widely from one solution to another of the same total concentration. Two changes then take place, a depolymerisation of the $(\text{HPO}_3)_n$ and a hydration of HPO_3 , of which the former is probably the quickest. The latter change (hydration) does not, as in the reaction studied by Sabatier, follow exactly the same exponential law until all the acid is changed. The two changes are seen most clearly in the Γ , K curves, Fig. 3, and from these it also appears that the conductivity of HPO_3 is considerably greater than that of H_3PO_4 .

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, March 18th, 1909.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows, the summaries here printed having been supplied by the authors for use at the meeting:—

"An Attempt to Detect some Electro-optical Effects." By HAROLD A. WILSON, F.R.S.

The paper contains a description of some experiments made with the object of detecting possible effects due to electric and magnetic fields and moving matter on the velocity of propagation of light in glass. The results obtained were negative, but it seems worth while to publish a short account of the experiments.

The optical part of the apparatus is a simple form of interferometer, which proved very easy and convenient to work with. It consists of a square glass frame made up of glass bars of square cross-section, cemented together with Canada balsam.

"On the Influence of their State in Solution on the Absorption Spectra of Dissolved Dyes." By S. E. SHEPARD, D.Sc.

(a) In the aqueous solutions of certain dye-stuffs—iscyanines, pinacyanols, cyanine—the dye is present partially or wholly in colloid solution, and the absorption spectrum is quite different from that of the true solution. The influence of various agencies, as heat, acid and alkali, electrolytes, on the absorption was examined quantitatively.

(b) In other dye solutions, the change from true solution to the colloid state is accompanied by broadening and diffusion of the absorption curve, consequent on the increase in number and size of the colloid particles. Deviations from Beer's law result.

(c) The state of dyes in solid media is comparable with that in liquid, and the absorption spectrum is similarly affected. The absorption of a number of dyes by membranes was studied.

(d) The solution of dyes appears to be a combined process of disaggregation of the solute, accompanied by a progressive combination with the solvent. If the same

stage of solution is attained in *different* solvents, the absorption maxima are displaced according to Kundt's law.

"*The Ferments and Latent Life of Resting Seeds.*" By JEAN WHITE.

The resting seeds of cereals such as wheat, maize, barley, oats, and rye all contain diastatic, fibrin-digesting, and ereptic ferments in appreciable amount. These ferments retain their activity without appreciable change in stored dry seeds for twenty or more years, that is long after the power of germination has been lost, which takes place in wheat after eleven to sixteen years, barley eight to ten years, oats five to nine years, maize and rye over five years.

No relation was noted between the vitality of seeds and the persistence of enzymes in them, but since the enzymes persisted longer than the power of germination, the question as to whether germination could take place in the absence of any pre-existent enzymes remains to be answered. In any case no otherwise non-germinable seeds could be excited to germination by the addition of any kind of enzyme, and where the germination was feeble the addition of enzymes usually lowered the percentage germination and often delayed germination also to some extent.

The erepsin appears to be more abundant than the pepsin, but otherwise in the cases of all three ferments greater differences are shown between different samples of the same age than between different seeds, or between the same seeds of varying ages. Pepsin appears, however, to be more abundant in rye than in any other cereal and is almost absent from maize. Dry oats, barley, and wheat can in part resist a temperature of 99–100° C. for one to four and a-half hours; after six hours' exposure all are killed, but the ferments are apparently unaffected. All the ferments are destroyed after an hour's dry heat at 130–131° C. The erepsin appeared to be least (one hour at 124° C.), the erepsin more (one hour at 124–128° C.), and the diastase, especially of barley, most resistant to dry heat (one hour at 124–131° C.).

Two days' exposure to liquid air, although it delays the subsequent germination and may also decrease the percentage, did not absolutely destroy any of the seeds tested and did not appreciably affect the ferments in any of the cereals. The dry diastase of barley is therefore able to withstand a range of temperature of 200° C. to –130° C.; it is therefore thermally a highly stable chemical compound.

Many seeds, including all cereals, give off appreciable quantities of carbon dioxide when stored in the air-dried condition, but others show no signs of respiration whatever. The respiration of air-dried wheat is especially pronounced, but in practically all cases every sign of respiration ceases when the seeds are moderately desiccated, although in the case of large seeds like maize minute traces of carbon dioxide may continue to escape for a time.

CHEMICAL SOCIETY.

Ordinary Meeting, March 18th, 1909.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President,
in the Chair.

MESSRS. F. P. Dunn, J. T. Furnell, J. H. Jeffery, P. May, A. B. Robertson, and W. O. Wootton were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Albert Riley Blackburn, B.Sc., Marshville, Derby Road, Widnes, Lancs.; Walter Campbell, Albert House, Westcliff-on-Sea; Daniel Little Couch, 9, Charlmont Road, Tooting, S.W.; Edward Gordon Couzens, B.Sc., 47, Allfarthing Lane, Wandsworth; Francis Clifford Dyche-Teague, B.Sc., 8, Mount Road, Hendon, N.W.; Charles James Grist, Apsley House, Banstead, Surrey; Leonard Angelo Levy, B.A., B.Sc., 60, Priory Road, West Hamp-

stead, N.W.; Robert Müller, Royal College of Science, South Kensington, S.W.; Frederick Leigh Okell, care of Straits Trading Co., Singapore; John Webster, 44, Holme-wood Gardens, Brixton Hill, S.W.

A Certificate has been authorised by the Council for presentation to ballot under By-law I. (3) in favour of Mr. Henry Ernest John Bletcher, Winnipeg, Manitoba.

The PRESIDENT announced that those Fellows desirous of supporting the International Memorial to the late Marcelin Berthelot should forward their subscriptions to M. H. Bocquillon-Limousin, 2bis Rue Blanche, Paris.

Of the following papers, those marked * were read:—

*76. "*Liquid and Solid Radium Emanation.*" By ROBERT WHYTLAW GRAY and Sir WILLIAM RAMSAY, K.C.B.

In the course of some recent work on radium emanation, the authors have prepared this gas in a state of fair purity, and it appeared worth while trying to liquefy it by pressure. It was therefore introduced into a very fine-bore capillary tube of 0.08 mm. diameter, fitted in a compression apparatus of the kind used by Ramsay and Young, and compressed to a smaller volume. When sufficiently small, there was seen at the conical point of the tube a minute column of liquid, easily visible under low microscopic power. By altering the volume, more or less liquid could be condensed. In short, by transmitted light all the usual phenomena of condensing and evaporating a liquid were observed. The liquid is colourless, and indistinguishable from water, or from, say, liquefied argon or xenon. If, however, the illumination from behind be extinguished, and the tube be viewed by its own illumination, even in broad daylight, the liquid is visible as a greenish or bluish green phosphorescent layer, not very luminous, but more luminous than the gaseous layer. Its vapour pressures were measured at –10° (boiling-point of sulphur dioxide), 0° (melting-point of ice), 12.8° and 16.2° (atmospheric temperatures), and 47° (boiling-point of carbon disulphide). But the gas was not quite pure; pressure rose during condensation. Allowing approximately for this, Ramsay and Young's rule was made use of to calculate the vapour-pressure curve. The pressures and temperatures are as follows:—

P.	T.
100 mm.	–74.5°
200 "	–66.1
500 "	–53.6
760 "	–48.5
1000 "	–43.1
2000 "	–31.0
5000 "	–12.8
10,000 "	+1.5

These vapour pressures must be taken as only approximate. The density of the liquid could be estimated, too, with rough approximation, as about 7, assuming that of the gaseous emanation to be 100 times that of gaseous hydrogen; it is considerably higher than that of xenon, namely, 3.52.

This liquid, as remarked, is only feebly phosphorescent. But if cooled by touching the tube with cotton-wool moistened with liquid air, it turns brilliant; the colour changes to a bright steel-blue, and it blazes with light. Continued application of liquid air changes the colour, first to white, then to yellow, and finally to orange. Through the microscope, it looks like a brilliant little arc light. On removing the liquid air, the reverse change occurs; the orange light becomes yellow, then white, and then blue; and there seems to be some sort of disturbance in the tube, as if crystals of a solid were disintegrating; then appears the faintly phosphorescing liquid, and if the volume be large enough, the still more faintly phosphorescing gas. Transmitted light shows merely a colourless liquid, as before. These changes can be reproduced again and again; they were exhibited to several persons in the laboratory. There is no doubt that the substance which is brilliantly luminous is a solid.

In *Nature* (1909, lxxix., 457), Prof. Rutherford describes experiments in which he obtained such "a brilliant point of phosphorescent light"; and he measured the temperature at which the "initial condensation of the emanation" occurred at atmospheric pressure; he found it to be -65° . In the light of the above experiments, it is difficult to say what he was observing; probably, the solidifying-point of the emanation, although he speaks of having seen "small drops of liquid emanation on the walls of the capillary."

*77. "Optically Active Substances which contain no Asymmetric Atom." (Preliminary Note). By WILLIAM HENRY PERKIN, WILLIAM JACKSON POPE, and OTTO WALLACH.

The possible existence of optically active substances which contain no asymmetric atom in the molecule was foreseen many years ago by van't Hoff, but the attempts hitherto made to obtain such compounds have been unsuccessful. All the constitutional formulæ at present assigned to substances which exhibit optical activity in the liquid state indicate the presence of one or more asymmetric atoms in the molecule.

Some time ago Perkin and Pope (*Trans.*, 1908, xciii., 1082) synthesised 1-methylcyclohexylidene-4-acetic acid, $\text{CH}_3\text{H} > \text{C} < \begin{smallmatrix} \text{CH}_2\text{CH}_2 \\ \text{CH}_2\text{CH}_2 \end{smallmatrix} > \text{C} < \begin{smallmatrix} \text{H} \\ \text{CO}_2\text{H} \end{smallmatrix}$, and pointed out that, on the basis of the tetrahedral environment of the carbon atom in methane, this substance possesses an enantiomorphous molecular configuration, and should hence exist in optically active forms. The constitutional formula, however, comprises no atom which can be described as asymmetric, no matter which definition of an asymmetric atom be adopted. The authors have now succeeded in separating from the synthetic and optically inactive acid a pure optically active modification of 1-methylcyclohexylidene-4-acetic acid by the method described below.

To a hot aqueous solution of two molecular proportions of externally compensated sodium 1-methylcyclohexylidene-4-acetate is added a hot aqueous solution of very slightly less than one molecular proportion of brucine hydrochloride; during admixture alcohol is added in just sufficient quantity to prevent the solution becoming turbid owing to separation of any oily salt. On cooling and scratching with a glass rod, rather less than one-half of the acid separates as crystalline *brucine lævo-1-methylcyclohexylidene-4-acetate*, $\text{C}_{23}\text{H}_{26}\text{O}_4\text{N}_2\text{C}_9\text{H}_{14}\text{O}_2\cdot 2\text{H}_2\text{O}$, whilst most of the dextro-component of the acid remains in solution as sodium salt. After crystallisation from dilute alcohol to remove adherent mother-liquor, the pure salt is obtained in colourless needles melting at 97° ; it shows the specific rotatory power $[\alpha]_D -58.1^{\circ}$ in a 0.8 per cent alcoholic solution.

Lævo-1-Methylcyclohexylidene-4-acetic acid is obtained from the brucine salt by addition of hydrochloric acid to its hot aqueous solution; after crystallisation from light petroleum the optically active acid melts at 52.5° , and shows the specific rotatory power $[\alpha]_D -81^{\circ}$ in alcoholic solution. On treatment with fuming hydrobromic acid it yields the potentially inactive 4-bromo-1-methylcyclohexyl-4-acetic acid, $\text{CH}_3\text{H} > \text{C} < \begin{smallmatrix} \text{CH}_2\text{CH}_2 \\ \text{CH}_2\text{CH}_2 \end{smallmatrix} > \text{CBr}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which melts at 78° .

DISCUSSION.

Dr. TUTTON asked whether Prof. POPE had been able to measure the crystals, and if so, whether he had found them to belong, as usual in cases of optical activity, to one of the eleven enantiomorphous classes which exhibit lower symmetry than the maximum symmetry of their system.

Dr. MCKENZIE referred to the work of Marckwald and Meth in this connection. Reference was also made to the fact that the configurations assigned to the active inosites represent these compounds as not possessing an asymmetric atom.

Replying to Dr. Tutton, Prof. POPE stated that attempts were being made to examine derivatives of the active acid

goniometrically in order to ascertain whether Pasteur's law holds in connection with the crystalline form of substances which owe their optical activity to the new kind of asymmetry now discovered. In reply to Prof. Armstrong, it was observed that, although the molecule contains no asymmetric atom, an asymmetric system forms part of the molecular configuration, and that the optical activity arises from the enantiomorphism thus introduced. In connection with Dr. McKenzie's remarks, Prof. POPE observed that no doubt can now exist that the acid described by Marckwald as 1-methylcyclohexylidene-4-acetic acid is really 1-methylcyclohexene-4-acetic acid, the molecule of which contains an asymmetric carbon atom. The configuration assigned to inosite certainly contained asymmetric carbon atoms.

*78. "The Constituents of the Rhizome of *Apocynum androsaemifolium*." By CHARLES WATSON MOORE.

The material employed in this investigation was the rhizome of *Apocynum androsaemifolium*, Linné. An alcoholic extract of the rhizome, when distilled in a current of steam, yielded small amounts of an essential oil and acetovanillone. The non-volatile constituents of the rhizome, as obtained after treating the alcoholic extract with steam, consisted of a brown resin (A) insoluble in either hot or cold water; a brown resin (B) soluble in the hot aqueous liquid, but which was slowly deposited on standing; and material which remained dissolved in the cold aqueous liquid. The brown resin (A) yielded small quantities of ipuranol, $\text{C}_{23}\text{H}_{38}\text{O}_2(\text{OH})_2$ (m. p. $285-290^{\circ}$), and acetovanillone; palmitic, stearic, oleic, and linolic acids, and a large quantity of unsaponifiable material. From the latter, two new alcohols, *androsterol*, $\text{C}_{30}\text{H}_{49}\cdot\text{OH}$ (m. p. $208-210^{\circ}$) and *homoandrosterol*, $\text{C}_{27}\text{H}_{43}\cdot\text{OH}$ (m. p. 192°), were obtained, whilst the presence of a third alcohol was proved by the isolation of its bromoacetyl derivative (m. p. $265-268^{\circ}$). Androsterol yields an acetyl derivative (m. p. $212-214^{\circ}$), and a monobromoacetyl derivative (m. p. $228-230^{\circ}$). *Acetylhomoandrosterol* melts at 236° . The brown resin (B) yielded a further small quantity of acetovanillone. The portion of the alcoholic extract of the rhizome which was soluble in cold water, and from which the above described resins had been removed, contained large amounts of sugar and tannin. It yielded a quantity of acetovanillone (m. p. 115°), which was also present in the form of its glucoside, *androsin*, $\text{CH}_3\cdot\text{CO}\cdot\text{C}_6\text{H}_3(\text{O}\cdot\text{CH}_3)\cdot\text{O}\cdot\text{C}_6\text{H}_{11}\text{O}_5\cdot 2\text{H}_2\text{O}$ (m. p. $218-220^{\circ}$), and a new substance, *apocynamarin*, $\text{C}_{28}\text{H}_{36}\text{O}_6\cdot 2\text{H}_2\text{O}$ (m. p. $170-175^{\circ}$), which possesses an intensely bitter taste, is highly toxic, and represents the chief active constituent of the rhizome.

*79. "The Action of Phosphorus Pentachloride on the Methylene Ethers of Catechol Derivatives. Part IV. Derivatives of Dihydroxyphenyl-acetic, -glycollic, and -glyoxylic Acids." By GEORGE BARGER and ARTHUR JAMES EWINS.

Starting from ethyl 3:4-methylenedioxymandelate, which is more readily obtained from piperonalcyanohydrin than the corresponding acid (previously obtained by Lorenz, *Ber.*, 1881, xiv., 793), the authors have prepared a number of methylene ethers and cyclic carbonates related to 3:4-dihydroxymandelic acid, $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$, and to 3:4-dihydroxyphenylglyoxylic acid, $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$, and also these acids themselves.

3:4-Dihydroxymandelic acid and its derivatives are very soluble in water, quite unlike epinephrine (adrenaline), which also contains the complex $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CH}(\text{OH})\cdot$. Dihydroxymandelic acid is much less stable than the corresponding keto-acid.

*80. "Studies in the Azine Series. Part I. The Constitution of Safranine." By JOHN THEODORE HEWITT, SIDNEY HERBERT NEWMAN, and THOMAS FIELD WINMILL.

Phenosafrafranine has the composition of a salt (chloride) of phenylphenazonium. According to Berntsen the two amino-groups are symmetrically situated, whilst Witt

May I be allowed to call the attention of the author, and of readers of this book in general, to the following facts:—

1. In reply to my first criticism of his views, Mr. Le Bas tacitly admitted that the molecular heats of combustion of the hydrocarbons are *not*, in general, proportional to their valency numbers, since in the case of unsaturated hydrocarbons, constants (depending on the unsaturated links) were to be *added* to the heats calculated from the valency numbers (see CHEMICAL NEWS, xcvi., 58).

2. That a further criticism of Mr. Le Bas's hypothesis (CHEMICAL NEWS, xcvi., 136), in which I went fully into the question, did not receive a reply. This may, I presume, be taken as implying that Mr. Le Bas admits the validity of my criticism.—I am, &c.,

H. STANLEY REDGROVE.

The Polytechnic, Regent Street W.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

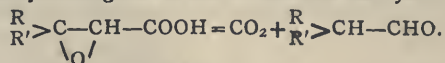
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlviii., No. 7, February 15, 1909.

Melting-point of Platinum.—C. Féry and C. Chéveneau.—Various investigators who have determined the melting-point of platinum have obtained results which differ by as much as 4.6 per cent. These differences appear to be due to the gaseous medium in which the fusion is performed. The authors' determinations also give a difference of 30 to 40° (1.7 to 2.3 per cent), which does not appear to be caused by a variation in the emissive power of platinum.

Thermal Phenomena accompanying the Action of Water on Aluminium Powder.—E. Kohn-Abrest and J. Carvallo.—When water acts on aluminium powder in the exothermic interval the grains of aluminium are attacked, yielding hydrated oxides of aluminium. Calorimetric measurement shows that the reaction sets free 8100 cal. for 4.82 grms. of pure aluminium, which would be about 90,000 cal. for a molecule of aluminium (Al₂). From the results of chemical analysis, the reducing power towards ferric sulphate, the amount of hydrogen set free when the powder is attacked by hydrochloric acid, the proportion of combined water, and the amount of oxygen fixed by the aluminium, it may be concluded that other oxides exist in the powder besides that of aluminium.

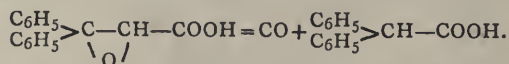
Catalytic Oxidation of Hypophosphorous Acid by Copper.—J. Bougault.—When sodium hypophosphite is treated with an excess of copper sulphate a brownish yellow precipitate is obtained; this appears to be a cuprous salt, probably the hypophosphite. It is gradually reduced to copper. In presence of an excess of hypophosphite a brown precipitate of the hydride is formed. On heating on the water-bath hydrogen is evolved, and a reddish precipitate is formed on the surface of the liquid. The hypophosphite is converted partially into phosphate and phosphite. The reaction slackens and finally stops before all the hypophosphite has been transformed. If the liquid is decanted and more hypophosphite is added hydrogen is again evolved. This operation can be repeated and a large quantity of hydrogen obtained with a small quantity of copper. Probably the water is decomposed in presence of the catalyser, hydrogen being evolved while the oxygen oxidises the hypophosphite.

Exception to the General Method of Preparing Aldehydes by means of Glycidic Acids.—René Pointet.—According to Darzens the glycidic acids liberated by a mineral acid from the products of the saponification of β-glycidic ethers with concentrated soda may be decomposed by heating into carbon dioxide and aldehyde—



With diphenylacetic aldehyde and its homologues this method gives very poor results. Diphenylglycidic acid

yields carbon monoxide and diphenylacetic acid when heated.



Similarly phenyltolylacetic ether gives phenyltolylglycidic acid when saponified, and the glycidic acid yields phenyltolylacetic acid on heating. Apparently the aldehyde is not formed owing to the presence of the two atoms of tertiary carbon in the neighbourhood of the CO group of the generating ketones.

Halogen Derivatives of γ-Oxycrotonic Acid.—MM. Lespieau and Viguière.—Bromine with γ-oxycrotonic acid yields an acid alcohol, CH₂OH—CBr=CBr—CO₂H, and a lactone, CH₂—CBr=CBr—CO. The lactone be-

longs to the maleic series, while the acid which is relatively stable towards heat and does not readily give lactone (except under the influence of reagents which frequently cause the transformation of a substance into a stereoisomer) belongs apparently to the fumaric series. It is quite easy to fix iodine by γ-tetrollic acid when the acid CH₂OH—CI=CI—CO₂H is formed.

MISCELLANEOUS.

Royal Institution.—The following are the lecture arrangements at the Royal Institution after Easter:—Prof. F. W. Mott, two lectures on "The Brain in Relation to Right-handedness and Speech"; Prof. Svante Arrhenius, two lectures on "Cosmogonical Questions" (the Tyndall Lectures); Prof. J. Garstang, two lectures on "The Hittites—(1) Monuments of Egypt and Asia Minor, (2) Recent Discoveries in Asia Minor and Northern Syria"; Dr. F. Gowland Hopkins, two lectures on "Biological Chemistry"; Mr. James Paterson, three lectures on "Aspects of Applied Aesthetics—(1) How a Fine Art Instinct may be best Developed, (2) Landscape Old and New, (3) Art and Ethics"; Mr. J. G. Millais, three lectures on Newfoundland; Prof. W. E. Dalby, two lectures on "A Modern Railway Problem—Steam v. Electricity"; Mr. R. T. Günther, two lectures on the Earth Movements of the Italian Coast and their Effects"; Prof. Walter Raleigh, two lectures on "(1) Edmund Burke, (2) Burke's Prose"; Dr. W. H. R. Rivers, two lectures on "The Secret Societies of Banks' Islands"; and Dr. F. F. Blackman, two lectures on "The Vitality of Seeds and Plants—(1) A Vindication of the Vitality of Plants, (2) the Life and Death of Seeds." The Friday Evening Meetings will be resumed on April 23, when Mr. Alexander Siemens will deliver a Discourse on "Tantalum and its Industrial Applications." Succeeding Discourses will probably be given by Dr. Edmund Gosse, Major Ronald Ross, Prof. G. E. Hale, Hon. Ivor Guest, Dr. J. Emerson Reynolds, Prof. J. A. Fleming, Prof. Sir James Dewar, and other gentlemen.

MEETINGS FOR THE WEEK.

MONDAY, 5th.—Royal Society of Arts, 8. (Cantor Lecture). "Steam Turbines," by G. Gerald Stoney.

— Royal Institution, 5. General Monthly Meeting. Society of Chemical Industry, 8. Mr. Watson Smith will exhibit and give a brief historic and chemical description of the now extinct Boghead Cannel Coal, or "Torban Hill Mineral." "Vapour Galvanising," by S. Cowper Coles. "Action of Sulphuric and Nitric Acids in the Nitration of Cellulose," by C. N. Hake and M. Bell.

TUESDAY, 6th.—Royal Society of Arts, 4.30. "Ceylon, its Industries and Material Progress," by Hon. John Ferguson.

WEDNESDAY, 7th.—Society of Public Analysts, 8. "New Standards for Sewage Effluents," by S. Rideal and W. T. Burgess. "Determination of the 'Oxygen Absorbed' by Sewage and Effluents by a Modification of Kubel's Method," by W. Carter. "Note on Enkabang and Teglam Fats and Katio Oil from Sarawak," by C. J. Brooks. "Composition of Milk," by H. D. Richmond.

THE CHEMICAL NEWS.

VOL XCIX., No. 2576.

THE THEORY OF DYEING.

By S. H. HIGGINS, M Sc.

PERHAPS there is no part of chemistry concerning which so many speculations have been made, and so few really quantitative experiments carried out than that portion dealing with the actions taking place during dyeing operations. Many observations have been made and deductions drawn, but yet there is a surprising lack, in this branch of applied chemistry, of the large amount of accurate work which is so characteristic of practically all other branches of chemical science. The art of dyeing is very old, for Pliny observed polygenetic colour dyeing and the application of different mordants; nevertheless, we have not progressed very far towards a true explanation of the phenomena observed during the dyeing of textile fibres.

The different theories which have been advanced may be divided into—(1) The Chemical Theory; (2) the Solution Theory; (3) the Mechanical Theory. It is true that other theories also exist of the nature of chemico-mechanical, but the above are the definite classes of opinion. The chemist with pardonable pride attempts to explain the process by saying that chemical combination takes place during dyeing, and that the product is mainly the result of chemical action between the fibre and the dye-stuff. He is imbued with the all-embracing nature of his science, and resembles the apostle of electrolytic dissociation who is busy attributing all chemical actions to the whims of those mysteries—the ions.

It is evident from the literature which is issued from time to time that most investigators of the dyeing process support the chemical theory; but it is also noticeable that most of their conclusions are based upon investigations of animal fibres, as silk and wool, whereas the actions taking place during the dyeing of vegetable fibres, as cotton and linen, have been left almost entirely without elucidation. It is maintained that silk and wool are capable of entering into definite chemical reactions with dye-stuffs, but whereas it is realised that cellulose, which is the chief constituent of vegetable fibres, cannot exhibit strong acidic or basic properties, yet the vegetable kingdom is left alone, and broad generalisations are made from experiments on the other fibres mentioned. At the outset it must be recognised that any theory of dyeing must include all classes of dyeing operations.

The solution theory was advanced in 1890 by Witt, and was the attempted application of the solid solution theory of physical chemistry to explain the phenomena observed during dyeing operations. This theory displayed the genius of its author, and afforded plausible explanations of many experiments, but in other respects it was found lacking. Witt drew attention to the fact that wool dyed with magenta was of the same colour as a water solution of magenta, and not the dark green colour of the magenta crystals. He said that this observation supported his contention that the magenta was dissolved in the wool. It was shown by Von Georgevics, however, that if magenta crystals are only made fine enough they also exhibit the red colour of the solution in water. Further, Walker and Appleyard, working with picric acid, made observations which were incompatible with Witt's conclusions, and thus the new theory of dyeing was shaken at its foundations.

The formation of theories is usually left to the greatest minds, to those of a philosophical turn, and it is possible that in this selection long experience of practical dyeing has seldom entered into the formulations.

The mechanical theory is to the effect that the dye-stuff is drawn from solution and held in some peculiar physical

manner by the fibre. Walter Crum gave a splendid exposition of this view in the sixties, but since that time chemical theory has been so much in evidence and chemical explanations so plausible that the process of dyeing has had to fall in and submit to the popular explanation. Nevertheless, on reading Crum's work one cannot help being struck with its merit, and one marvels that, in spite of this well-known work, the chemical theory of dyeing has gained so many adherents.

In support of the mechanical theory of dyeing some papers have recently been issued, e.g., Hübner, "Experimental Investigation of the Process of Dyeing" (*Trans. Chem. Soc.*, 1907). It is well known that charcoal and other solids possess the property of extracting dye-stuffs from solution; in the case of charcoal the tinting effect is not noticeable, but if a white substance, as China clay, be used, then it is seen that the solid is dyed. It has been stated that in such cases the dye-stuff can be wholly washed out by water, but Hübner showed that these solids behaved either like wool or like cotton during the treatment with water to remove the dye-stuff. Thus it was found that charcoal behaved similarly to wool during every treatment to which wool is submitted in commercial dyeing, and likewise graphite was found to fall in with the usual methods of dyeing cotton; in both cases the fastness to washing was similar.

In pursuance of this line of research the present writer has recently issued (Higgins, *Journ. Soc. Chem. Ind.*, 1909, xxviii., 188) an account of experiments which further support the mechanical theory of dyeing. Wool was beaten in a beating engine to five different states of division, and the samples obtained were dried. They were then allowed to absorb dye-stuff from solution and moisture from the air. It was found that the maximum absorption of dye-stuff and of moisture took place during, approximately, the same time, and that this maximum amount in both cases was practically constant for all states of division. Samples of cotton mercerised, bleached, and unbleached, were found to absorb iodine from weak potassium iodide solution in proportion as they absorbed moisture from the air. A striking result was obtained by plotting the moisture contents of cotton-yarn mercerised with different strengths of caustic soda solution. The moisture curve was found to closely resemble the dye trial curve obtained when a substantive cotton dye-stuff was used; in short, the mercerised cotton samples only absorbed more dye-stuff in so far as they absorbed more moisture. The experiments bring out a marked similarity between the absorption by textile fibres of a solid from a liquid medium, and of a vapour from a gaseous medium, and as the absorption of moisture from air is relegated to that class of little understood phenomena known as surface attraction, it must therefore be taken that the dyeing of textile fibres also belongs to that class of physical action.

THE FRUIT OF *VIBURNUM NUDUM*.

By ROBERT H. LOTT.

THE fruit of *Viburnum nudum* was gathered in the swampy portions of the territory around Sylvan Beach, New York, August 27 to September 5, 1907. It grows on shrubs four to seven feet in height. The species is common in swampy regions from the New England States to Florida. The portion gathered August 27 was comparatively green, while on the 4th and 5th of September it had become quite ripe. It was then a beautiful cardinal red, very abundant in the neighbourhood of Sylvan Beach, and the most gorgeous object in the early autumn landscape.

The dried fruit of this viburnum consists of berries that resemble commercial currants. They differ in that their colour is bluish black instead of brownish black, and they are more elongated. The odour of the berries is also similar to that of currants.

The taste of the berry passes quickly through different degrees of sweetness to that of a decided bitterness. The bitter taste is very similar to that of a wild cherry, or to the bark of a peach tree, although not quite so strong. The fruit when burned gives off three distinct odours; first, a sweet odour like that of toffy made from sorghum molasses; secondly, an odour somewhat resembling coffee; and lastly, the odour of burning damp straw or leaves, which is very penetrating. The fruits are very easily crushed in an agate mortar. There were 270 grms. available for the analysis. The weight of each was 0.05 of a gm.

The Sugars.

About 100 grms. of the fruit were taken for the sugar extraction. They were placed in a 500 cc. flask, fitted with an inverted condenser, and treated with successive portions of alcohol for about thirty-five days. The alcoholic extraction was removed each day, and a fresh portion applied. The alcohol was distilled off, and two substances remained behind: one a dark, thick syrup, the other a resinous gummy substance possessing a bluish clay colour. The alcoholic extraction gave an acid reaction to litmus-paper. The colour and odour of the first extraction bore a strong resemblance to that of fresh cider. In a short time this odour changed to that of old cider, and a test for acetic acid showed that fermentation was taking place.

A test with Fehling's solution at the end of thirty-five days showed that the sugars were almost extracted, and distilled water was substituted for alcohol. The berries under the alcohol treatment remained hard, but on the addition of water they became soft and mushy. The alcoholic extraction at the end of the thirty-five days was almost colourless, while the water extraction was very black, resembling coffee that had been boiled. Ten days more were required to remove all coloration and the remainder of the sugars by the water treatment.

The percentage of the sugars was determined by Fehling's solution of such a strength that 10 cc. corresponded to 0.05 gm. sugar. The determination was made by taking 1 cc. of the sugar extraction and diluting with 50 cc. of distilled water in a small beaker. This was heated to boiling and titrated with Fehling's solution. To ascertain when the end-point was reached a small portion of the solution was filtered from time to time, always pouring the filtrate back, until the sugars had no more reducing power. The filtrate was of a marked straw-colour until the reduction was complete, at which time it became a light blue. The change in colour could be brought about in either direction by three drops of the sugar solution or the same of Fehling's solution, and so it seemed a satisfactory test. There was found to be 42.85 grms. of sugar corresponding to 42.85 per cent. The loss by fermentation was not ascertained.

The two different sugar extractions were evaporated to dryness, and the odour was that of scorched sorghum. The residue was a black thick jelly-like substance, and had the bitter taste of the original berry.

A portion of this residue was purified by heating for several hours on the water-bath with purified bone-black. The solution was quite light in colour, and was evaporated to dryness for treatment with phenylhydrazine.

With portions of 0.01 gm. sugar, 0.04 gm. phenylhydrazine, and 0.03 gm. sodium acetate the test pointed to fructose. Another test with cobalt nitrate indicated dextrose, so it is quite likely that both are present. The osazone crystals were purified by crystallising with alcohol, and attempts were made to obtain the melting-point, but the efforts were unsatisfactory.

The residue of the fruits after the sugar extraction was dried and weighed. The loss of weight was 53 per cent. The berries were black in colour, shrivelled, and hard.

As a larger quantity of residues was needed for oil extraction, it seemed likely that the sugars might be removed more rapidly, by using a litre flask and larger quantities and changing the solvent twice daily. In two weeks all

the sugar in 125 grms. of berries was extracted. This portion was dried and weighed, showing a loss of 48 per cent as compared with 53 per cent the first time.

The Ash.

Four different portions of the berries of about 2 grms. each were ashed in a platinum evaporating dish of 100 cc. capacity. From the first portion the silica, iron, aluminium, calcium, and magnesium were determined; from the second portion, the sodium and potassium by a modification of the J. Lawrence Smith method; from the third portion, the sulphates; and lastly, the phosphates. The analysis showed more sodium than potassium, and the flame-test both from the original berry and the sugar syrup pointed in the same direction. The results of the analyses were as follows:—

First Portion.

SiO ₂		2.11	per cent of the ash.
Al ₂ O ₃		3.88	" "
Fe ₂ O ₃		3.88	" "
CaO		7.66	" "
MgO		1.87	" "
Weight of berries taken		2.015	gm.
Weight of the ash	..	0.09	"

Second Portion.

K ₂ O		12.87	per cent of the ash.
Na ₂ O		16.789	" "
Weight of berries	..	2.0403	grms.
Weight of ash	..	0.0933	"

Third Portion.

SO ₃		27.14	per cent of the ash.
Weight of berries	..	2.0533	grms.
Weight of ash	..	0.0921	"

Fourth Portion.

The phosphate was determined by dissolving the ash in nitric acid, filtering, and treating the filtrate with a solution of ammonium molybdate.

P ₂ O ₅		12.89	per cent of the ash.
Weight of berries	..	2.0523	grms.
Weight of ash	..	0.0734	"

The total is 89.09 per cent of the ash, the remainder is organic matter that escaped combustion, and carbon dioxide.

A portion of the pulp of the berries after the sugar and oil extractions was thoroughly dried, and 2.6083 grms. ashed. The ash weighed 0.0483 gm., about half the weight of the ash of the original fruit, and a much larger bulk of fruit was required to weigh 2 grms. than of the original fruits. The pulp now had only two characteristic odours, that of coffee and of damp burning leaves. The odour of toffy seemed to have disappeared.

The Oils.

The dried berries from the sugar extraction weighing 112 grms. were finely ground in a small coffee mill, and used for the oil extraction. The powder was placed in a 500 cc. flask, which was tightly fitted with an inverted condenser, and treated with ether. Two weeks were required to extract all the oil. The ether was removed from the oil by distillation. The oil at first was of a beautiful green colour, due no doubt to chlorophyll. The attempt was made to remove the chlorophyll by filtering through bone-black, with ether, in the cold, but no effect whatever could be detected. The oil was then heated for twelve hours with ether and bone-black, and then filtered. The oil now came out a beautiful amber colour, the specific gravity of which was 0.9353. It was not possible to solidify it in a freezing mixture. The boiling-point is about 82°. It has a characteristic odour which somewhat resembles

that of olive oil. Four saponifications were made by Koetstorfer's method, which resulted as follows:—

	Amount taken.	Time heated.	Saponification equivalent.
1.	0.857 grms.	2	612
2.	0.858 "	4	343
3.	2.302 "	12	291
4.	3.1605 "	16	303

The results indicate that the oil is difficult to saponify, and that complete saponification takes place only after continued heating. The figures show that the oil is one of the oleins in the same group as castor oil, almond oil, and olive oil. The result coincides well with the physical characteristics.

The products of the third saponification were separated. The soapy solution after saponification was diluted with distilled water and a quantity of ether was added, which dissolved the unsaponifiable portion. This was separated from the liquid, evaporated to constant weight, and found to be 0.0483 gm. This residue was dissolved in hot alcohol and filtered, and left to evaporate spontaneously. A few minute crystals separated out which were supposed to be cholesterol.

After separating the ethereal layer the remaining liquid was acidified with sulphuric acid and slightly heated, whereupon the fatty acids liberated by saponification collected upon the top of the liquid. These were separated and boiled with distilled water for several hours. They were afterwards separated from the water, dried on the water-bath, and found to weigh 3.6033 grms., more than the amount of oil at first taken. The increase in weight is due, doubtless, to the oxidation of the acids. Two distinct acids appeared, one very clear and odourless which crystallised in a freezing mixture to fine needles and melted at about 4°; the other was a yellow limpid liquid, with an odour resembling lard. This last crystallised at a low temperature, but we did not succeed in finding the melting-point. Judging from the descriptions given in the literature the clear acid seems to be oleic, and the yellow one linoleic. Both reacted acid to litmus-paper.

An attempt was made to obtain the weight of the soluble fatty acids. The acidified liquid first separated from the insoluble fatty acids, and the distillate exactly neutralised by normal caustic soda, using phenolphthalein as an indicator. The washings from the insoluble acids were now added to the contents of the flask and again distilled to a small bulk. This distillate also was neutralised with normal caustic soda. The two distillates were evaporated to dryness to constant weight. The number of centimetres used in the neutralisation was multiplied by 0.022 and the product subtracted from the constant weight. The result was unsatisfactory. Each fruit bears a single flat stone which undoubtedly contains the oils.

The Proteins.

Some of the berries were crushed and boiled in distilled water for a short time. A small amount of this solution was heated with nitric acid, giving a yellow colour, which became an orange-red when made alkaline. This showed the presence of albumen.

A portion of the fruit was heated with an excess of soda-lime in a dry test-tube. The fumes reacted alkaline to litmus-paper. A similar effect was produced by heating the berries alone at a high temperature.

The nitrogen was determined by the Kjeldahl method. 2.0933 grms. of the berries gave 0.0112 gm. of nitrogen, equivalent to 0.53 per cent.

A quantity of solution which resulted from boiling the berries in distilled water was tested to learn if the albumen contains sulphur. We treated a solution of lead acetate with caustic soda until the precipitate which first forms is re-dissolved. The fruit solution was now added to this and heated to boiling. A dark coloured precipitate of lead sulphide formed, which indicated the presence of sulphur.

The Acids.

The acid tests were made from the sugar extraction. Tartaric and citric acids were found with a small quantity of malic acid. Citric acid seemed to predominate.

I desire to express my thanks to Dr. N. Knight for many suggestions.

Cornell College, March 11, 1909.

RECENT RESEARCHES IN RADIO-ACTIVITY.*

By Prof. ERNEST RUTHERFORD, M.A., LL.D., D.Sc., F.R.S.

IN 1904 I had the honour of giving an Address at the Royal Institution on the subject of radio-activity. In the interval steady and rapid progress has been made in unravelling the tangled skein of radio-active phenomena. In the present lecture I shall endeavour to review very shortly some of the more important advances made in the last few years, but as I cannot hope to mention, even briefly, the whole additions to our knowledge in the various branches of the subject, I shall confine my attention to a few of the more salient facts in the development of which I have taken some small share.

In my previous lecture I based the explanation of radio-active phenomena on the disintegration theory put forward in 1903 by Rutherford and Soddy, which supposes that the atoms of the radio-active bodies are unstable systems which break up with explosive violence. This theory has stood the test of time, and has been invaluable in guiding the experimenter through the maze of radio-active complications. In its simplest form, the theory supposes that every second a certain fraction (usually very small) of the atoms present become unstable and explode with great violence, expelling in many cases a small portion of the disrupted atom at a high speed. The residue of the atom forms a new atomic system of less atomic weight, and possessing physical and chemical properties which markedly distinguish it from the parent atom. The atoms composing the new substance formed by the disintegration of the parent matter are also unstable, and break up in turn. The process of degradation of the atom, once started, proceeds through a number of distinct stages. These new products formed by the successive disintegrations of the parent matter are in most cases present in such extremely minute quantity that they cannot be investigated by ordinary chemical methods. The radiations from these substances, however, afford a very delicate method of qualitative and quantitative analysis, so that we can obtain some idea of the physical and chemical properties of substances existing in an amount which is far below the limit of detection of the balance or spectroscopy.

The law that governs the breaking up of atoms is very simple and universal in its application. For any simple substance the average number of atoms breaking up per second is proportional at any time to the number present. In consequence, the amount of radio-active matter decreases in a geometrical progression with the time. The "period" of any radio-active product, *i.e.*, the time for half the matter to be transformed, is a definite and characteristic property of the product which is uninfluenced by any of the laboratory agents at our command. In fact, the period of any radio-active product, for example, the radium emanation, if determined with sufficient accuracy, might well be taken as a definite standard of time, independent of all terrestrial influences.

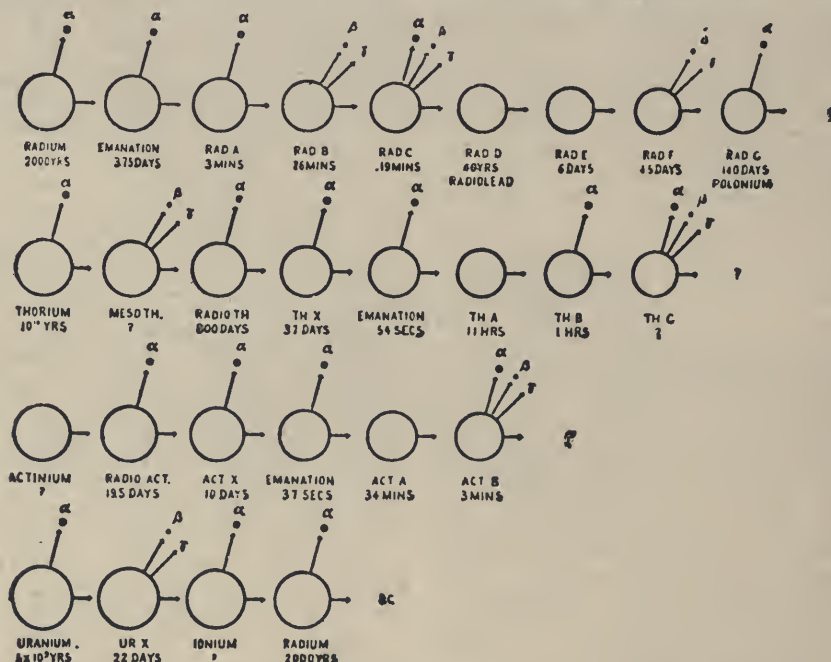
The law of radio-active transformation can be very simply and aptly illustrated by an hydraulic analogy. Suppose we take a vertical cylinder filled with water, with an opening near the base through which the water escapes through a high resistance. (A short glass tube in which is placed a plug of glass-wool is very suitable). When the discharge is started, the amount of water escaping per

* A Discourse delivered at the Royal Institution, January 31, 1908.

second is proportional to the height of water above the zero level of the cylinder. The height of water decreases in a geometrical progression with the time in exactly the same way as the amount of radio-active matter decreases. We can consequently take the height of the column of water as representing the amount of radio-active matter A present at any time. The quantity of water escaping per second is a measure of the rate of disintegration of A and also of the amount of the new substance B formed per second by the disintegration of A. The "period" of the substance is controlled by the amount of resistance in the discharge circuit. A high resistance gives a small flow of water and a long period of transformation, and *vice versa*. By a suitable arrangement we can readily trace out the decay curve for such a case. A cork carrying a light vertical glass rod is floated on the water in the cylinder. A light camel's hair brush is attached at right angles, and moves over the surface of a smoked-glass plate. A vertical line drawn on the glass through the point of contact of the brush gives the axis of ordinates, while a horizontal line drawn through the brush when the water has reached its lowest level gives the axis of abscissæ. If the glass plate

in the cylinder B is traced out in the same way as before by moving the glass plate at a constant rate across the tracing brush. If the period of A is very long compared with that of B the water is supplied to B at a constant rate, and the water in B reaches a constant maximum height when the rate of supply to B equals the rate of escape from the latter. The curve traced out in that case is identical in shape with the "recovery curve" of a radio-active product supplied at a nearly constant rate. The quantity of matter reaches a maximum when the rate of supply equals its own rate of transformation. The relative height of the columns of water in A and B represents at any time the relative amounts of these substances present.

If the period is comparable with that of B, the height of water in B after reaching a maximum falls again, since as the height of A diminishes, the supply to B decreases. Ultimately, the height of B will decrease in a geometrical progression with the time at a rate corresponding to the longer period of the two. This is an exact illustration of the way the amount of a radio-active substance B varies when initially only the parent substance A is present. By



is moved with uniform velocity from the moment of starting the discharge, a curve is traced on the glass which is identical in shape with the curve of decay of a radio-active product, where the ordinates at any time represent the relative amount of active matter present, and the abscissæ time. With such an apparatus we can illustrate in a simple way the increase with time of radio-active matter B, which is supplied by the transformation of a substance A. This will correspond, for example, to the growth of the radium emanation with time in a quantity of radium initially freed from emanation. Let us for convenience suppose that A has a much longer period than B. In the hydraulic analogy A is represented by a high head of water discharging at its base through a circuit of high resistance into the top of another cylinder representing the matter B. The water from the cylinder B escapes at its base through a lower resistance. Suppose that initially only A is present. In this case the water in the cylinder B stands at zero level. On opening the stopcock connecting with A, water flows into B. The rise of water with time

using a number of cylinders in series, each with a suitable resistance, we can in a similar way illustrate in a quantitative manner the variation in amount with time of a number of products arising from successive disintegrations of a primary substance. By suitably adjusting the amount of resistance in the discharge circuits of the various cylinders, the curves could be drawn to scale to imitate approximately the variation in amount of the various products with time when the initial conditions are given.

During the last few years a very large amount of work has been done in tracing the remarkable succession of transformations that occur in the various radio-active substances. The known products of radium, thorium, actinium, and uranium are shown graphically above, together with the periods of the products and the character of the radiations they emit. It will be seen that a large list of these unstable bodies are now known. It is probable, however, that not many more remain to be discovered. The main uncertainty lies in the possibility of overlooking a product of rapid transformation following or succeeding

one with a very slow period. In tracing out the succession of changes, the emanations or radio-active gases continuously evolved by radium, thorium, and actinium have marked a very definite and important stage, for these emanations can be easily removed from the radio-active body, and their further transformations studied quite apart from the parent element. The analysis of the transformation of the radium emanation has yielded results of great importance and interest. After passing through three stages, radium A, B, and C, of short period, a substance, radium D, of long period, makes its appearance. This is transformed through two stages E and F of short period into radium G, of period 140 days. Meyer and Schweidler have conclusively shown that radium D is the primary constituent of the radio-active substance separated by Hofmann, and called by him radio-lead. Radium G is identical with the first radio-active substance separated from pitchblende by Mme. Curie, viz., polonium. We are thus sure that these bodies are transformation products of radium. It will be seen that I have added another product of period 4.5 days between radium D and polonium. The presence of such a product has been shown by Meyer and Schweidler.

In the case of thorium, a very long list of products is now known. For several years thorium X was thought to be the first product of thorium, but Hahn has recently shown that at least two other products of slow transformation intervene, which he has called mesothorium and radiothorium. The radiothorium emits α -rays, and has a period of more than 800 days. Mesothorium apparently emits β -rays, and has a still longer period of transformation, the exact value of which has not yet been accurately determined. Since thorium is used commercially on a large scale, there is every prospect that we shall soon be able to obtain considerable quantities of very active preparations of mesothorium and radiothorium. The separation of these bodies from thorium does not in any way alter its commercial value. It is to be hoped that if these active preparations are separated in quantity, the physicist and chemist may be able to obtain a supply of very active material at a reasonable cost, and that there will not be an attempt to compete with the ridiculously high prices charged for radium.

From the radio-active point of view, the radio-elements are only distinguished from their families of products by their comparatively long period of transformation. Now we have reason to believe that radium itself is transformed according to the laws of other radio-active products with a period of about 2000 years. If this be the case, in order to keep up its supply in a mineral, radium must be produced from another substance of relatively long period of transformation. The search for this elusive parent of radium has been one of almost dramatic interest, and illustrates the great importance of the theory as a guide to the experimenter. The view that radium was a substance in continuous transformation was put forward by Rutherford and Soddy in 1903. The most probable parent of radium appeared to be uranium, which has a period of transformation of the order of 1000 million years. If this were the case, uranium, initially freed from radium, should in the course of time grow radium, i.e., radium should again appear in the uranium. This has been tested independently by Soddy and Boltwood, and both have shown that in carefully prepared uranium solutions there is no appreciable growth of radium in the course of several years. The rate of production of radium, if it occurs at all, is certainly less than 1/1000th of the amount to be expected from theory. This would appear at first sight to put out of count the view that uranium is the parent of radium. This, however, is by no means the case, for such a result could be very easily explained if one or more substances of very slow period of transformation appeared between uranium and radium. It is obvious that the necessity of forming such an intermediate product would greatly lengthen the time required before an appreciable amount of radium appeared.

There is, however, another indirect but very simple method of attack to settle the parentage of radium. If radium is derived from the transformation of uranium, however many unknown products intervene, the ratio between the amount of radium and uranium in old minerals should be a definite constant. This is obviously the case, provided sufficient time has elapsed for the amount of radium to have reached its equilibrium value. The constancy of this relation has been completely substantiated by the independent work of Boltwood, Strutt, and McCoy. It has been shown that the quantity of radium corresponding to 1 grm. of uranium is 3.8×10^{-7} grm., and is the same for minerals obtained from all parts of the world. Since the radium is always distributed throughout the mass of uranium, we cannot expect to find nuggets of radium like nuggets of gold, unless by some chance the radium has been dissolved out of radio-active minerals and re-deposited within the last few thousands of years. To those who had faith in the disintegration theory, this unique constant relation between the amounts of two elements was a satisfactory proof that radium stood in a genetic relation with uranium. A search was then made for the unknown intervening product which, if isolated, must grow radium at a rapid rate. A year or so ago Boltwood observed that a preparation of actinium separated from a uranium mineral did grow uranium at a constant but rapid rate. It thus appeared as if actinium were the long-looked-for parent of radium, and that actinium and its long family of products intervened between uranium X and radium. I was, however, able to show that actinium itself was not responsible for the growth of radium, but another unknown substance separated with it. These results were confirmed by Boltwood, who finally succeeded in isolating a new substance from uranium minerals, which was slowly transformed into radium. This substance, which he termed "ionium," has apparently chemical properties similar to those of thorium, and emits α rays of penetrating power less than those of uranium.

The main previsions of the theory have thus been experimentally verified. Radium is a changing substance the amount of which is kept up by the disintegration of another element, ionium. In order to complete the chain of evidence, we require to show that uranium grows ionium, and it is probable that evidence in this direction will soon be forthcoming. We thus see that we are able to link uranium, ionium, radium, and its long line of descendants, into one family, with uranium as its first parent. As uranium has a period of transformation of more than one thousand million years, it will not be profitable at the moment to try and trace back the family further.

It appears almost certain that, from the radio-active point of view, uranium and thorium must be considered as two independent elements. The case of actinium is different, for Boltwood has shown that the amount of actinium in minerals, like the amount of radium, is proportional to the amount of uranium. This indicates that actinium stands in a genetic relation with uranium. Unless our experimental evidence is at fault, it does not appear probable that actinium belongs to the main line of descent of uranium, for the activity of actinium separated from a mineral compared with radium is only about one-quarter of what we should expect under such conditions. I think that a suggestion which I put forward some time ago may account for the obvious connection of actinium with uranium, and at the same time for the anomaly observed. This supposes that actinium is a branch descent from some member of the uranium family. It does not appear improbable that at one stage of the disintegration two distinct substances may be produced, one in greater quantity than the other. After the expulsion of an α particle, it may happen that there are two possible arrangements of temporary stability of the residual atom. The great majority of the atoms may fall into one arrangement, and the remainder into the other. Actinium in this case would correspond to the substance in lesser quantity. It would

act as a distinct element, and would break up in a different way from the main amount. It is probable that a large amount of accurate work will be required before the position of actinium in the scheme of changes can be fixed with certainty. It is a matter of remark how closely actinium resembles thorium in its series of transformations. It would appear that the atom of actinium has many points in common with thorium, or rather with its product, mesothorium.

The recent observations on the growth of radium offer very simple and straightforward method of determining experimentally the period of radium. Suppose that we take a uranum mineral and determine by the emanation method the quantity of radium contained in it. If the immediate parent of radium (*i.e.*, ionium) is next completely separated from the uranum and radium, it will begin to grow radium at a constant rate. Now the rate of growth of radium observed is a measure of the rate of breaking up of the radium parent in the mineral, since before separation the rate of production was equal to the rate of breaking up. Now the growth of radium observed for a short interval, for example, a year, divided by the quantity present in the mineral, gives the fraction of the radium breaking up per year. Proceeding in this way, Boltwood found that the fraction breaking up per year is about $1/3000$ th, and that the period of radium is about 2000 years—a value which lies between the most probable values deduced from quite distinct data.

From an inspection of the radio-active families, it will be seen that out of twenty-six radio-active substances that have been identified, seventeen give out α -rays or α - and β -rays, four give out only β -rays, and five emit no rays at all. The rayless and β -ray products are transformed according to the same law as the α -ray products, and there is the same sudden change of physical and chemical properties as the result of the transformation. In the case of the substances which throw off atoms of matter in the form of α particles, there are obvious reasons for anticipating a change in properties of the substance, but this is not the case for the rayless or β -ray products. We must either suppose that the mass of the atom is not appreciably changed by the transformation, which consists in an internal re-arrangement of the parts of the atom, or that the atom expels a particle at too low a velocity to be appreciated by the electrical methods. Unfortunately, it is very difficult to study the rayless products with care, as in practically every case they are succeeded by a ray product of comparatively rapid transformation. The rayless products are of great interest as indicating the possibility of transformations which can occur without any detectable radiation.

In the course of the analysis of radio-active changes, special methods have been developed for the separation of the various products from each other. It is only in a few cases, however, that we can hope to obtain a sufficient quantity of the substance to examine by means of the balance. It should be possible to obtain workable quantities of actinium, radium D (radio-lead), and radium G (polonium), but the isolation of these substances in any quantity has not yet been effected. Sir William Ramsay and Mr. Cameron have made a number of important investigations of the properties and volume of the radium emanation, freed so far as possible from any traces of known gases. The remarkable initial contraction of the volume due to the emanation shows that there is still much to be done to obtain a clear understanding of the behaviour of this intensely radio-active gas when obtained in a pure state.

Simultaneously with the work on the analysis of radio-active changes, a large number of investigations have been made on the laws of absorption by matter of the three primary types of radiation from active matter, *viz.*, the α -, β -, and γ -rays, and the secondary radiations to which they give rise. It has generally been accepted for some years that the γ -rays are a type of penetrating X-rays. The latter are supposed to consist of electro-magnetic

pulses in the ether, set up by the impact or escape of electrons from matter, and akin in many respects to very short waves of ultra-violet light. Recently, however, Bragg has challenged this view, and has suggested that the γ -rays (and probably also the X-rays) are mainly corpuscular in character, and consist of uncharged particles, or "neutral pairs," as he terms them, projected at a high velocity. Such a view serves to explain most of the experimental observations equally well as the pulse theory; Bragg has recently brought forward additional evidence, based on the direction of the secondary radiation from the γ -rays, which he considers to be inexplicable by the pulse theory. We must await further data before this important question can be settled definitely, but the theory of Bragg, which carries many important consequences in its train, certainly deserves very careful examination.

(To be continued).

ON THE RATE OF EVOLUTION OF GASES FROM HOMOGENEOUS LIQUIDS.*

By V. H. VELEY, F.R.S.

PART I.

("Nam nil ægrius est quam res secernere apertas ab dubiis, animus quas ab se protinus addit."—LUCRETIVS, *De Rerum Natura*, iv., 467.

In a series of papers the conditions of evolution of gases, as products of chemical changes from homogeneous liquids, have been discussed. The cases examined have been the formation of nitrous oxide from molten ammonium nitrate (*Journ. Chem. Soc.*, 1883, 370), of carbonic oxide from formic and sulphuric acids and incidentally of other reactions (*Phil. Trans.*, 1888, clxxix., A, 257), of nitrogen from aqueous solutions of ammonium nitrite (*Journ. Chem. Soc. Trans.*, 1903, 736). Finally, the several cases and conditions were discussed (*Phil. Mag.*, 1903, [6], viii., 271), but as this last publication appears to have escaped the notice of authors of recent papers, though not of writers of recent text-books on Physical Chemistry, it may be worth while to recapitulate very briefly the points there set forth. The initial delay, so frequently observed, is referred to the effects of two different causes—(1) the formation of intermediate compounds, and (2) the storage of gas manufactured in the liquids.

To take monomolecular reactions, for example, the differential equations are—

$$dx/dt = (k - k_1c) \dots \dots \dots (1)$$

$$d(x-z)/dt = kc \dots \dots \dots (2)$$

and the final state of affairs is simply represented—

$$dx/dt = kc \dots \dots \dots (3)$$

In (1) k_1 is the lag factor due to the formation of intermediate compounds, or opposing side reaction, and (2) z is the proportion of gas retained; the other symbols have their usual significance.

It would appear that recent writers have attributed results which are the conjoint effect of causes (1) and (2) solely to that of (2), so that the amount of gas estimated to be retained is wholly out of proportion to the total quantity which could be manufactured from the mass of material used. It may also be desirable to point out that the criterion of the effect of cause (2) only is that the times Δt for the evolution of unit volumes of gas or the volumes Δv_x evolved in unit time decrease *uniformly*; when this is not the case, then the conjoint effect of (1) and (2) must be considered.

The purpose of the present paper is to discuss several cases from these points of view, utilising results obtained by other workers and myself.

I. Carbonic Oxide from Formic and Sulphuric Acids.

It has been shown (*cf. supra*) that the volume of gas stored varied from 3×8 to $49 \cdot 4$ cc., when the total volume

* A Paper read before the Faraday Society, March 2, 1909.

which could be manufactured was about 150 cc., and from 72.6 to 76 cc. with a total manufacture of 330 cc. (the volumes of the mixture being approximately the same); and also that the greater proportion, as it should be according to theory, took place in the first few intervals of time, while in the remaining interval the total amount was approximately a few cc. only.

It has been generally supposed by other writers besides myself that under such conditions a supersaturated solution of gas is formed; unfortunately, there are no data of the solubility of carbonic oxide in diluted sulphuric acid, but as recent writers have (as I conceive) been led to exaggerate such a degree of supersaturation, I adduce the following calculations from the only data available.

The equivalent weight of water of solution used = $260 \times 1.8 + 83 = 551$ grms. (*vide infra*) would dissolve at 80° C. and 760 mm., according to the estimations of Winkler (*Zeit. Phys. Chem.*, 1892, ix., 171), 5.65 mgrms. carbonic oxide; taking the density of the gas as identical with that of nitrogen 76 cc. (the maximum volume retained) at 80° C. and 760 mm. weigh 69.5 mgrms.; therefore the degree of supersaturation in terms of water, the only data available, = $69.5/5.65 = 12.5$, and the average of all determinations would be less than 10.

It was also shown that the decomposition of formic acid (or its salts) by sulphuric acid was in accordance with a bimolecular section—

$$dx/dt = k(a-x)^2 \text{ or } dx/dt = k(a-x)(b-x) \quad (4);$$

but recently this same reaction has been investigated by Lamplough (*Camb. Phil. Soc.*, 1908, xiv., 591), who under conditions, other than temperature, totally different found it to be of a monomolecular type.

In consequence of this discrepancy I have calculated out the several masses of materials used by Lamplough and myself (selecting one typical mixture from each), converting cc. into grms. by sulphuric acid density tables, taking densities of sodium formate solution as = 1, and referring the several masses to the same standard of 1 gm. sodium formate. The comparison works out as follows:—

	Lamplough's mixture (1).	Veley's mixture (2).
Sulphuric acid ..	2.9 grms.	260 grms.
Water	142 "	83 "
Sodium formate	1 "	1 "

The proportion of sulphuric acid to water in (1) is about 1:50 or 3:150, but in (2) is 3:1, or, in other words, mixture (1) was 150 times more dilute than (2).

But from equations—

$$dx/dt = k_1(a-x) \rightarrow \log a(a-x) = k_1t \quad (5)$$

and—

$$dx/dt = k_2(a-x)(b-x) \rightarrow \log a(b-x)/b(a-x) = k_2t \quad (6).$$

If x is small compared with b (in this particular case the proportion of water), then practically $b = b - x$, and a reaction of the strictly bimolecular type* would approximate to the monomolecular type which is the result arrived at by Lamplough.

(In the paper alluded to above I may reasonably take exception to the following sentence: "David M. Lichty had shown . . . that the decomposition of oxalic acid by sulphuric acid is a unimolecular reaction and not bimolecular as found by Veley." To criticise work which I have never done, and conclusions at which I have never arrived, appears to apertain rather to the realm of romance than to the sober polity of science).

II. Nitrogen from Ammonium Nitrite.

As pointed out before, Harcourt many years ago observed an initial delay, due either wholly or partly to retention of nitrogen gas when mixed solutions of sodium nitrite and ammonium chloride were heated. Arndt's (*Zeit. Phys. Chem.*, 1901, xxxix., 64) results in certain series of experiments point to a similar phenomenon for solutions obtained from barium nitrite and ammonium

sulphate, which still contained barium sulphate in suspension. As methods have been now devised for obtaining ammonium nitrite in a fair degree of purity, it might be of interest to determine the degree of supersaturation of nitrogen gas as comparable with that deduced from experiments with the diazonium salts.

III. Oxygen from Hydrogen Peroxide Solutions.

Some few results obtained by Bredig and Muller v. Berneck (*Zeit. Phys. Chem.*, 1899, xxxi., 258) in their investigations of the decomposition of hydrogen peroxide solution with colloidal platinum, point to a slight retention of oxygen gas, but it is believed that they, as Lamplough, purposely avoided supersaturation by keeping the solutions in agitation. Such results are not, therefore, available for this communication, the object of which is to show that the degree of supersaturation of liquids by gases manufactured therein by a process of chemical change probably has been greatly over-estimated.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 18th, 1909.

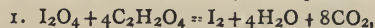
Sir WILLIAM RAMSAY, K.C.B., F.R.S., President,
in the Chair.

(Concluded from p. 167).

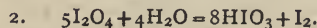
84. "Iodine Dioxide." By MATTHEW MONCRIEFF PATTISON MUIR.

Reference was made to the work of Millon, in 1844, and of Kämmerer, in 1861, on an oxide of iodine said to be composed of iodine and oxygen united in the ratio of I:2O, none of which work satisfactorily proved the existence of the compound.

The compound IO_2 , or I_2O_4 , has been prepared by the dehydration and partial deoxidation of iodic acid by heating that acid with concentrated sulphuric acid. Two methods of analysing iodine dioxide were described. It was shown that the interactions of this oxide and oxalic acid, in the presence of sulphuric acid, at 100°, and with boiling water, are severally represented by the equations:—



and—



Iodine dioxide is a pale yellow, crystalline solid of specific gravity 4.2; it is decomposed at about 130° into iodine and oxygen. The molecular weight of the compound has not been determined. The reactions of the oxide with acids and with various reagents were described; in most of these interactions, iodine pentoxide and iodine are produced. Iodine dioxide is slightly soluble in cold concentrated sulphuric acid; 100 cc. of the acid dissolve 1.54 grms. of the oxide at 15° to 20°. Inasmuch as iodine dioxide forms a compound with sulphur trioxide having the composition $\text{I}_2\text{O}_4 \cdot 3\text{SO}_3$, the oxide has slightly basic properties. This compound is not decomposed by heating to 100°, but begins to give off iodine, oxygen, and sulphur trioxide at about 120°.

Incidentally, it was shown that iodic anhydride and sulphur trioxide combine, when heated together at 100°, to form a compound which has the composition $\text{I}_2\text{O}_5 \cdot 2\text{SO}_3$.

The slightly basic characters of the two oxides of iodine emphasise the connections between iodine and manganese.

85. "A Polarimetric Method of Identifying Chitin." By JAMES COLQUHOUN IRVINE.

A solution of chitin in concentrated hydrochloric acid is slowly transformed into glucosamine hydrochloride at the ordinary temperature. The change is greatly accelerated

* I am indebted to Mellor, "Chemical Statics and Dynamics," London, 1904, for this simple proof.

by keeping the solution at 45°, being then complete in eight to ten hours. Under these conditions, the hydrolysis is quantitative, no humic compounds or other colouring matters are produced, and thus the reaction may be followed polarimetrically. As chitin is levorotatory, the conversion into glucosamine hydrochloride is accompanied by a characteristic "inversion," the average result (calculated on the initial concentration) being:—

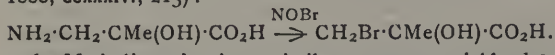


The results obtained showed great uniformity, and thus the method can be applied as a test for chitin, which is capable of positively identifying 0.1 grm. of the substance.

The constancy of rotatory power observed with specimens of chitin prepared from widely different sources affords strong evidence that the substance is a definite compound of uniform composition and structure. As "spongin" and "keratin" did not show any optical inversion during hydrolysis, it seems doubtful if these substances are in any way related to chitin. The different formulæ suggested for the latter compound have been examined in their relationship to the polarimetric results, the best agreement being given by the expression $(C_{30}H_{50}O_{19}N_4)_n$, in which aminoglucose and acetylamino-glucose residues are present in the proportion of one to three.

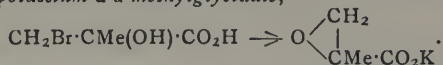
86. "The Conversion of d- α -Methylisoserine into d- α -Methylglyceric Acid." By FRANCIS WILLIAM KAY.

In the course of investigating the action of nitrosyl bromide on the β -amino-acids, it was found that α -methylisoserine (β -amino- α -hydroxyisobutyric acid) was converted into β -bromo- α -methyl-lactic acid (β -bromo- α -hydroxyisobutyric acid), which melts at 102–103° (uncorr.), and has already been described by Melikoff (*Annalen*, 1886, ccxxiv., 213):—



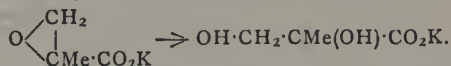
d- α -Methylisoserine by a similar treatment yields d- β -bromo- α -methyl-lactic acid, which crystallises from benzene in needles, m. p. 114° (uncorr.), and has $[\alpha]_{D 20} + 7.40^\circ$ in approximately 10 per cent aqueous solution.

The action of the theoretical amount of alcoholic potassium hydroxide (2 mols.) converts the above bromo-acid into potassium d- α -methylglycidate,—



This salt crystallises in silvery leaflets, and has $[\alpha]_{D 20} - 17.57^\circ$.

When potassium d- α -methylglycidate is heated with water to 100°, it undergoes hydroxylation, and is transformed into potassium d- α -methylglycerate,—



The aqueous solution of this salt has a specific rotation of -4.00° .

87. "The Action of Steam on Iron." (Preliminary Note). By JOHN ALBERT NEWTON FRIEND.

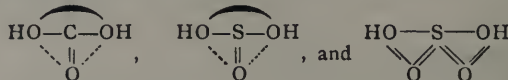
The author has studied the action of steam on iron at temperatures ranging from 100° to a red heat. It is found that pure carbon dioxide-free steam has no action on pure iron until those temperatures are reached at which the steam begins to dissociate, when a black oxide (presumably Fe_3O_4) is produced.

The conclusion is drawn that the usual statement that steam is decomposed by red-hot iron is not true. The reaction really takes place in two stages, involving (i.) the dissociation of the steam, and (ii.) combination of the iron with the dissociated oxygen.

88. "The Constitution of Sulphurous, Sulphuric, Carbonic, and Formic Acids." By JOHN ALBERT NEWTON FRIEND.

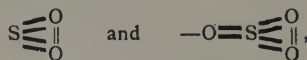
In a recent communication, Miss Smedley (*Trans.*,

1909, xcv., 231) has discussed the constitution of the carboxyl group, and incidentally suggests that carbonic, sulphurous, and sulphuric acids may be represented by the schemes:—

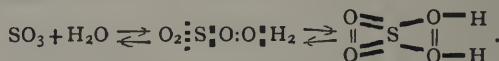


The instability of the first two acids is attributed to the symmetrical arrangement of the third atom of oxygen between two hydroxyl groups.

The present author considers, however, that such an explanation is not sufficient. Arguing along similar lines it would be expected that an acid containing a fourth atom of oxygen between three hydroxyl groups would be too unstable to exist, but orthophosphoric acid, $PO(OH)_3$, is comparatively very stable. Evidence has already been adduced (Friend, *Trans.*, 1908, xciii., 266) to show that the molecules of sulphur di- and tri-oxides are most probably correctly represented by the schemes:—

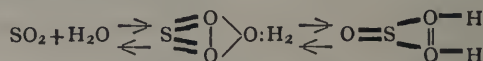


where the thick lines represent the free valencies, and the thin, the latent valencies. Since the latent valencies of the third oxygen atom in the trioxide are unsaturated, the latter readily combines with water to form a stable hydrate, which then undergoes more or less complete rearrangement to sulphuric acid until equilibrium is attained:—

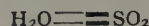


Since the hydrate is exceedingly stable, there is little tendency for the reactions to proceed from right to left hence the stability of the sulphuric acid.

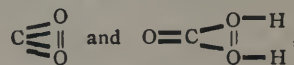
With sulphur dioxide, however, the case is different. The latent valencies of the two oxygen atoms mutually saturate each other, and there is little tendency for a hydrate to form; hence equilibrium is obtained according to the following schemes:—



when only a small quantity of the hydrate is present, and the relative concentration of the sulphurous acid can therefore never be great. This would account for the instability of the acid, and the fact that its solution exhibits all the properties of the dioxide. It might appear at first sight that, since sulphur dioxide is unsaturated, a hydrate of the type—



might be formed. This is, however, not possible, as the free valencies of the sulphur are positive, whereas one of the latent valencies of the oxygen is positive and the other negative (Friend, *loc. cit.*). Carbon dioxide and carbonic acid may be represented by the schemes:—



and a similar explanation for the instability of the acid holds. In formic acid a carboxylic group is present, and the latent valencies of the two oxygen atoms mutually saturate each other, thus:—

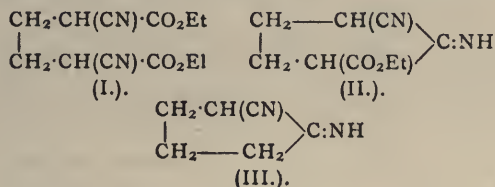


That carbon monoxide does not dissolve in water to form formic acid is explained by the fact that the free and latent valencies of the oxygen atom saturate the four free valencies of the carbon atom, a saturation which is rendered possible by the amphoteric nature of the latter (Friend,

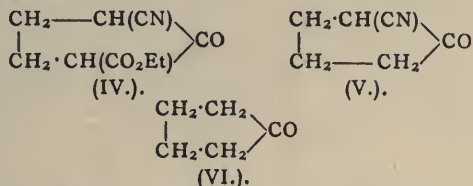
loc. cit.); hence it is not until some vigorous method is adopted for breaking this connection, as, for example, the action of the gas on heated potassium hydroxide, that formic acid can be prepared.

89. "The Formation and Reactions of Imino-compounds. Part IX. The Formation of Derivatives of Cyclopentane from $\alpha\delta$ -Dicyano-derivatives of Butane." By STANLEY ROBERT BEST and JOCELYN FIELD THORPE.

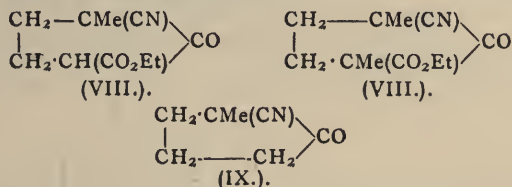
When ethylene dibromide reacts with dry ethyl sodio-cyanoacetate (compare *Trans. Chem. Soc.*, xxxi., 17) in benzene solution, ethyl $\alpha\delta$ -dicyanoadipate (I.) is formed, and this compound is readily transformed into ethyl carbonate and ethyl 2-imino-3-cyanocyclopentane-1-carboxylate (II.), from which 1-imino-2-cyanocyclopentane (III.) can be easily obtained.



These imino-compounds are hydrolysed by cold mineral acids, yielding ethyl 5-cyanocyclopentan-1-one-2-carboxylate (IV.), and 2-cyanocyclopentan-1-one (V.) respectively, whilst further treatment with acids yields, in both cases, cyclopentanone (VI.).

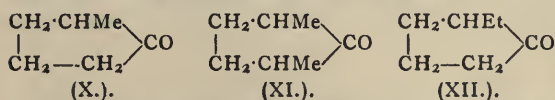


The methylation of ethyl 5-cyanocyclopentan-1-one-2-carboxylate (IV.) leads to the formation of ethyl 5-cyano-5-methylcyclopentan-1-one-2-carboxylate (VII.) and ethyl 5-cyano-2:5-dimethylcyclopentan-1-one-2-carboxylate (VIII.); the first-named compound, on hydrolysis, is transformed into 2-cyano-2-methylcyclopentan-1-one (IX.), which is identical with the compound prepared by the methylation of 2-cyanocyclopentan-1-one (V.).



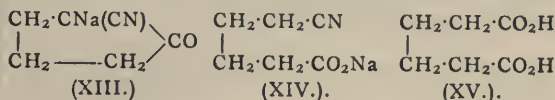
The ethylation of ethyl 5-cyanocyclopentan-1-one-2-carboxylate (II.) yields a mixture consisting of four parts of the O-ethyl derivative and one part of the C-ethyl derivative.

The cyclopentane ring in these compounds is stable towards acid hydrolysing agents, and therefore 2-methylcyclopentan-1-one (X.), 2:5-dimethylcyclopentan-1-one (XI.), and 2-ethylcyclopentan-1-one (XII.) can be readily obtained from the compounds mentioned above.



The ring is, however, readily broken by the action of alkalis, the final product in every case being either adipic acid or an alkyl derivative.

Probably the most remarkable instance of the instability of the cyclopentane ring under these conditions is afforded by the sodium derivative of 5-cyanocyclopentan-1-one (XIII.), which dissolves in water, forming the sodium salt of δ -cyanovaleic acid (XIV.), from which adipic acid (XV.) can be obtained on further hydrolysis.



90. "The Preparation of Methyl 1:1-Dimethylcyclopentan-3:4-dione-2:5-dicarboxylate." By JOCELYN FIELD THORPE.

Methyl 1:1-dimethylcyclopentan-3:4-dione-2:5-dicarboxylate, $\text{CMe}_2\text{CH}(\text{CO}_2\text{Et})\text{—CH}(\text{CO}_2\text{Et})\text{—CO}$, was first prepared

and identified by Dieckmann (*Ber.*, 1899, xxxii., 1934), the method used for its preparation being the interaction of ethyl oxalate and methyl $\beta\beta$ -dimethylglutarate in the presence of sodium ethoxide. Dieckmann prepared this substance with the expressed object (*loc. cit.*, p. 1935) of ultimately obtaining from it by reduction and by methylation and reduction acids of the same formulæ as those proposed by Bredt for camphoric acid and apocamphoric acid, but he remarks (*loc. cit.*, p. 1933) that the yield of the dimethyl salt is exceedingly small.

Dieckmann was evidently unable to overcome the initial difficulties occasioned by this poor yield, as the syntheses proposed by him were ultimately accomplished by Komppa (*Ber.*, 1901, xxxiv., 2472; 1903, xxxvi., 4332).

In the first of these papers (*Ber.*, 1901, xxxiv., 2473) Komppa stated that he had succeeded in obtaining an "almost quantitative yield" of methyl-1:1-dimethylcyclopentan-3:4-dione-2:5-dicarboxylate from ethyl oxalate and methyl $\beta\beta$ -dimethylglutarate. He omitted to mention, however, either in his paper on apocamphoric acid or on camphoric acid, the conditions under which this increased yield could be obtained.

During the past two years the author has made numerous experiments with the object of reproducing the conditions employed by Komppa, because it was desired to prepare a quantity of this methyl salt for the purpose of another investigation, but in no one of these experiments has the yield exceeded 10 per cent of the theory.

In view of this difficulty, and of the fact that private communications with Prof. Komppa have been unsuccessful in obtaining the details of this important preparation, the author suggests that, as eight years have now elapsed since the publication of Komppa's paper on apocamphoric acid, and six years since he published his preliminary paper on the synthesis of camphoric acid, publication of the full experimental details is highly desirable.

91. Condensation of Cyanohydrins. Part I. Condensation Products from Anisaldehydecyanohydrin and Cinnamaldehydecyanohydrin." By HAMILTON McCOMBIE and ETHEL PARRY.

Minovici (*Ber.*, 1899, xxxii., 2206) described the action of dehydrating agents on anisaldehydecyanohydrin as resulting in the production of a compound melting at 146°, to which he assigned the formula $\text{CH}_3\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{CN})\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_3$. This substance has now been shown to be 2:5-di-*p*-methoxydiphenyloxazole, $\text{N}=\text{C}(\text{C}_6\text{H}_4\cdot\text{OMe})\text{—O}$, which was originally described by Minovici himself (*Ber.*, 1896, xxix., 2100), and its formation in this reaction is due to the presence of unchanged aldehyde in the cyanohydrin.

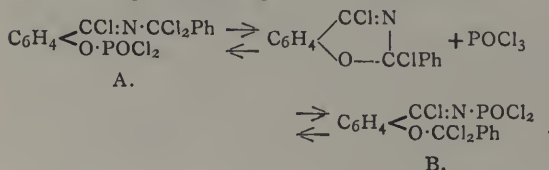
When pure anisaldehydecyanohydrin is subjected to the action of gaseous hydrogen chloride, two substances are formed, namely, (1) a compound melting at 156°, the constitution of which is to be more fully investigated, and (2)

3-keto-2:5-di-p-methoxydiphenyl-3:4-dihydro-1:4-diazine,
 $N \equiv C(C_6H_4 \cdot OMe) \cdot CO$
 $N \equiv CH:C(C_6H_4 \cdot OMe) > NH$ (compare Japp and Knox,
Trans., 1905, lxxxvii., 701).

Cinnamaldehydecyanhydrin, on being subjected to the action of gaseous hydrogen chloride, yields 3-keto-2:5-distyryl-3:4-dihydro-1:4-diazine.

92. "Labile Isomerism among the Acylsalicylamide, Acylhydroxyamine, and Phenylbenzomotoxazine Groups." By ARTHUR WALSH TITHERLEY and WILLIAM LONGTON HICKS.

In order to throw fresh light on the mechanism underlying the wandering of acyl groups in derivatives of salicylamide and aromatic o-hydroxyamines, the behaviour of phenylbenzomotoxazine with phosphorus pentachloride has been studied; and evidence has been obtained that the resulting 2:4-dichlorophenylbenzomotoxazine under the influence of phosphoryl chloride exhibits tautomeric behaviour owing to wandering of chlorine atoms, thus:—



A bright yellow crystalline substance is obtained which is decomposed by water, yielding benzoysalicylonitrile, but by 98 per cent sulphuric acid yielding N-benzoysalicylamide. As the same yellow solid is produced by the action of phosphorus pentachloride on benzoysalicylonitrile, it must be regarded either as a mixture of A and B, or one of these in a labile form.

In the production of the yellow substance from phenylbenzomotoxazine, various by-products are obtained, among which the double compound of phosphoryl chloride

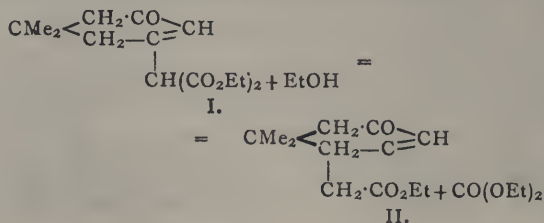
and 4-chlorophenylbenzomotoxazine, $C_6H_4 \begin{array}{l} \swarrow CCl:N \\ \searrow O \cdots CHPh \end{array}$, appears to be present. Benzylidene chloride is also produced in considerable quantity together with chlorophosphorus derivatives of salicylonitrile.

93. "The Alkyl Compounds of Platinum." By WILLIAM JACKSON POPE and STANLEY JOHN PEACHEY.

The authors have continued the investigation of the salts derived from trimethylplatonic hydroxide, $(CH_3)_3Pt \cdot OH$, concerning which they have already published a preliminary note (*Proc.*, 1907, xxiii., 86).

94. "Note on the Preparation of Trimethylcyclohexenone, (Isophorone) from Ethyl Malonate and Chlorodimethylcyclohexenone." By ARTHUR WILLIAM CROSSLEY and CHARLES GILLING.

In a recent communication (*Trans.*, 1909, xcv., 20) it has been shown that when the sodium compound of ethyl malonate acts on 5-chloro-1:1-dimethyl- Δ^4 -cyclohexen-3-one, the condensation product does not consist of the substance having Formula I., as might have been expected, but of ethyl 1:1-dimethyl- Δ^4 -cyclohexen-3-one-5-acetate (II.). The formation of this latter compound necessitates the elimination of a carbethoxy-group, and it has now been proved that the reaction affords another instance of the production of ethyl carbonate during such condensations:—



(compare Thorpe, *Trans.*, 1905, lxxxvii., 1681; also *Proc.*, 1909, xxv., 17; Leuchs and Geserick, *Ber.*, 1908, xli., 4171).

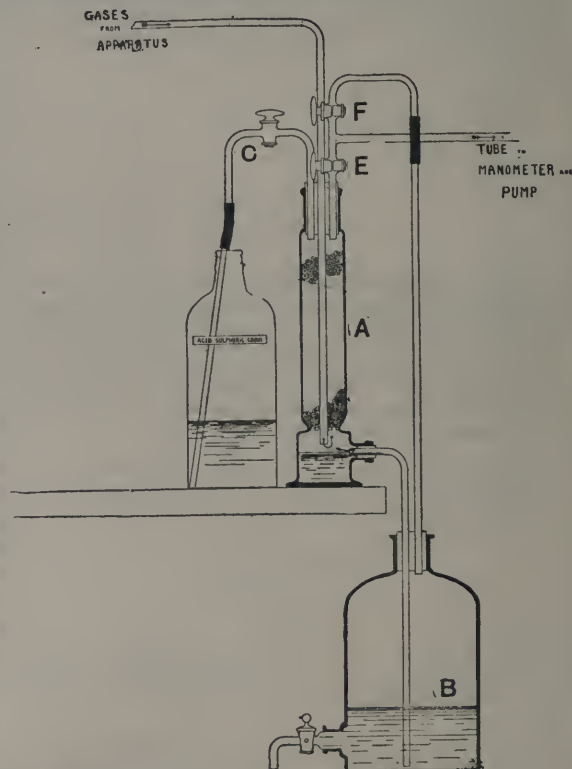
Twenty-four grms. of chlorodimethylcyclohexenone were treated with ethyl malonate as already described (*loc. cit.*, p. 23). The steam distillate was extracted with ether, the ethereal solution dried, evaporated, and the residual 28 grms. of liquid fractionally distilled, using a column. After three distillations, 7.5 grms. of a liquid with an ethereal odour were obtained, boiling constantly at 126°, and giving the following numbers on analysis:—

0.1927 gave 0.3575 CO_2 and 0.1471 H_2O . $C = 50.59$;
 $H = 8.48$. $C_5H_{10}O_3$ requires $C = 50.84$; $H = 8.47$ per cent.

This data prove the substance to be ethyl carbonate.

95. "A Simple Gas-drying Apparatus for Use with a Mechanical Exhaust Pump." By GEORGE STANLEY WALPOLE.

It is found convenient in chemical laboratories to use a mechanical exhaust pump for many purposes, especially in conjunction with distillation apparatus. To maintain the pump in such a condition that at any moment it is capable of working at its maximum efficiency, it must be kept dry by use of either a steam-jacket or else an efficient drying apparatus interposed between it and the still.



The accompanying drawing represents a form of desiccator which has been in use continuously for some months under somewhat severe conditions.

The gases from the still pass directly down the tower A. If the tap E be closed and F open, they pass through the concentrated sulphuric acid in the reservoir B. This is the arrangement when the still is being exhausted at the commencement of distillation, or when only a moderate vacuum is required. If the tap F is closed and E opened, the gases pass up the tower, meeting a slow stream of sulphuric acid running over the glass beads and regulated by tap c.

In this arrangement, a short circuit is thus established which eliminates the hydrostatic pressure of the sulphuric acid in the bottle B, and there is no resistance offered to the gases passing to the pump. It is advisable to leave all taps turned off when the apparatus is not in use. The acid from B can be run out periodically, and if suitable, used again.

(We are indebted to the Chemical Society for the loan of the woodcut illustrating this paper).

96. "Some Esters of Antimony Trioxide." By JOHN FRANCIS MACKEY.

Lang, MacKey, and Gortner (*Trans.*, 1908, xciii., 1364) described a new method for the esterification of arsenious oxide with the aliphatic alcohols and with phenol and its homologues, and expressed the opinion that similar esters might be obtained from antimony trioxide and the same alcohols and phenols. In the present work attempts have been made to form these esters by treating a mixture of antimony trioxide and the alcohol or phenol in the following ways:—(1) Heating under a reflux condenser; (2) heating with Soxhlet attachment and anhydrous copper sulphate; (3) heating in sealed tubes at 150°; (4) heating with metallic calcium; (5) treating with anhydrous copper sulphate in the cold. By the second method, yields of from 3 per cent in the case of ethyl antimonite to 15 per cent in the case of isobutyl antimonite, and of 40 per cent in the case of phenyl antimonite to 48 per cent in the case of *m*-tolyl antimonite were obtained. By heating with metallic calcium a yield of 60 per cent was obtained with phenyl antimonite. The following esters were isolated in quantity:—*Methyl, ethyl, propyl, isobutyl, amyl, isoamyl, phenyl, o-, m-, and p-tolyl antimonites*. The aliphatic esters are all liquids, which decompose on heating at atmospheric pressure into antimony trioxide and the alcohol from which they were prepared, whilst phenyl, *o*-tolyl, and *p*-tolyl antimonites are solids melting at 13°, 16°, and 14° respectively. The boiling-points of these esters, under 30 mm. pressure, are as follows:—*Methyl, 65°; ethyl, 115–120°; propyl, 143°; isobutyl, 144°; amyl, 170°; isoamyl 163°; phenyl, 250°; o-tolyl, 352°; m-tolyl, 300°; and p-tolyl, 345°*. They are soluble in absolute alcohol, ether, chloroform, or benzene, but decompose immediately on the addition of water into antimony trioxide and the alcohol from which they were prepared. Accurate methods of analysis have been worked out for both the esters of the aliphatic alcohols and the esters of phenol and its homologues. On analysis these esters were found to correspond with the general formula R_3SbO_3 .

MANCHESTER LITERARY AND PHILOSOPHICAL SOCIETY.

Ordinary Meeting, March 23rd, 1909.

Prof. A. SCHUSTER in the Chair.

The following papers were read:—

"On the Moving Force of Terrestrial and Celestial Bodies in relation to the Attraction of Gravitation." By Dr. HENRY WILDE, F.R.S.

Reference was briefly made by the author to the historic controversy which exercised the minds of distinguished men of science and learning, for more than two centuries, as to whether the force of a body in motion by the free action of gravity is simply as the velocity, according to Descartes and Newton, or as the square of the velocity in agreement with Leibnitz, and proved experimentally by Smeaton, Wollaston, Ewart, Dalton, Joule, and others. But no attempts have been made to extend the results of these experiments to the motions of celestial bodies. The author has demonstrated that the moving force and the attraction of gravitation are alike inversely proportional to the square of the distance, and are correlated equally in amount to maintain and retain the moon and other celestial bodies in their orbits during their revolutions round their primaries.

"The Action of Hydrogen on Sodium." By ALFRED HOLT, jun., M.A.

Some experiments were described on the action of hydrogen on sodium which, when considered with the work of Moissan and of Troost and Hautefeuille, point to the conclusion that the hydride, Na_2H , described by these latter authors, should probably be regarded as a solid solution of the hydride, NaH , in sodium, and not as a definite compound.

The hydrogen first reacts with the metal to form the hydride, NaH , which dissolves in the excess of sodium as a complex $NaH-Na$. More and more of this complex is formed as the temperature is raised, but at the same time it dissociates with increasing rapidity into hydride and sodium.

As the formation of this complex would reduce the vapour pressure of the hydride, NaH , very little of this compound could be obtained till the dissociation pressure of the complex exceeded its vapour pressure. This occurs about 470° C., and about 430° C. the hydride, NaH , begins to decompose rapidly into hydrogen and sodium.

Some specimens of the white crystalline hydride, NaH , were exhibited.

"Differences in the Decay of the Radium Emanation." By Prof. E. RUTHERFORD, F.R.S. (in conjunction with Mr. Y. TUOMIKOSKI).

CORRESPONDENCE.

THE INSTITUTE OF CHEMISTRY AND RESEARCH WORK.

To the Editor of the Chemical News.

SIR,—As Prof. Kipping's letter referring to my recent Presidential Address at the Annual Meeting of the Institute of Chemistry is based on his perusal of an abstract only, I should be glad to have the opportunity of adding a few words which may indicate more precisely the attitude which I take up with regard to his suggestion that "good research work in the case of all candidates for the Fellowship" should be made compulsory.

Although I am quite prepared to admit that it would be desirable that "Fellows" should possess greater capacity and higher attainments than are demanded of "Associates" of the Institute, it does not appear to me possible, under present conditions, to base this higher qualification on the candidate's research record. It not unfrequently happens that the research work performed is of a private and confidential character, and that its value cannot therefore be judged by the Council of the Institute or by any similar tribunal. The machinery for recognising published research work already exists in the shape of the D.Sc. degrees of the several universities and in the Fellowship of the Royal Society, but this machinery can take no cognisance of confidential investigations such as might be performed in connection with a chemical industry.

Dr. Kipping apparently agrees with me that such confidential researches may, and often do, involve both originality and attainments of the highest order, but he does not make any suggestion as to how the chemist who has conducted such research shall establish his claim for admission to the Fellowship. Were the Institute therefore to impose such a restriction upon the Fellowship, it would be necessary for those chemists who are engaged in confidential investigations also to carry out independent publishable research work in order to qualify for the higher diploma, which would be accessible to the academic chemist without any such additional burden. The injustice involved in such an arrangement is manifest.

As a matter of fact, even under the present regulations the Fellowship does imply more mature attainments than does the Associateship, in that the regulations prescribe

that "every Associate applying for admission to the Fellowship is required to produce evidence that he has since his admission as an Associate, and for a period of three years therefrom, been continuously engaged in the study and practice of chemistry in a manner that shall be satisfactory to the Council." It is by a progressive interpretation and administration of this clause that the Council can, in my opinion, most judiciously raise, and, I trust, in course of time will raise, the dignity of the Fellowship more and more above that of the Associateship qualification. In the meantime the Council has systematically been increasing the stringency of the requirements for the Associateship, and has been successful in building up a chemical qualification which in some respects is quite unique, not having its counterpart in any university diploma.

The strenuous endeavours of the Council, which have been effective in gradually but steadily raising the standard of the Institute qualification to its present position, are, in my opinion, deserving of the sympathy and gratitude of the great body of chemists in this country, and I therefore particularly regret that Prof. Kipping should have thought fit to publicly disparage the work of the Institute.—I am, &c.,

PERCY F. FRANKLAND.

University of Birmingham,
March 31, 1909.

NOTICES OF BOOKS.

The Theory of Valency. By J. NEWTON FRIEND. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1909.

THE appearance of a complete treatise on valency will be welcomed by English chemists, for hitherto the literature of the subject has been restricted to scattered articles in periodicals and the transactions of the scientific societies. This work not only discusses general theories and the history of their development, but also goes fully into the question of the valencies of individual elements. Moreover, since the Periodic System is the most satisfactory basis of classification, it is treated in some detail. The chapter on the exceptions to the Periodic Law is particularly clear and very interesting. With the exception of carbon, to which an entire chapter is devoted, the valencies of the elements included in each group are considered together. The book is a valuable addition to the series of Text Books of Physical Chemistry to which it belongs, and no higher praise can be given to it than to say that it is quite up to the level of excellence of the earlier volumes of the same series.

Alloys and their Industrial Applications. By EDWARD F. LAW. London: Charles Griffin and Company, Ltd. 1909.

IN the earlier chapters of this book a succinct account is given of the properties, constitution, and methods of investigation of alloys in general, while in addition the most important alloys are treated individually in considerable detail. The book is not intended chiefly for the student of metallurgy, but aims rather at being helpful to the practical man, whether engineer or manufacturer; hence it has been made as little technical as possible. At the same time it is refreshing to observe that the "practical man" is not, as so often in books of this nature, thought likely to be quite devoid of any general scientific knowledge, and the treatment is not popular, some rather complicated or abstruse aspects of the subject being treated very clearly. The book contains many reproductions of photomicrographs, for all of which magnifications of 100 or 1000 diameters have been employed. Thus they may very readily be compared. In addition, two interesting colour photographs are given of grey iron and phosphor-bronze; these have been taken by the author on Lumière autochrome plates, and are the first examples of the application of colour photography to metallography.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

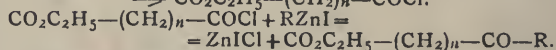
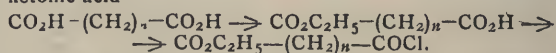
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlviii., No. 8, February 22, 1909.

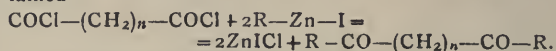
Atomic Weight of Potassium.—G. D. Hinrichs.—Expressed in terms of the author's unit ($\frac{1}{12}$ C diamond) and assuming that when C = 12, O = 16, the atomic weights of the elements are generally whole numbers. For some the fraction $\frac{1}{2}$ must be added, but the author has not met with any for which the fraction is $\frac{1}{4}$. Potassium is the only example of an element for which $\frac{1}{2}$ has to be added.

Chloralic Acids.—M. Hanriot.—Chloraloses (the compounds of chloral with sugars) when oxidised give chloralic acids. These acids give lactones when treated with acetyl chloride and zinc chloride. From the author's experiments it appears that only mannose gives an oxidation product, which contains C₈ and is a lactone. All other chloraloses are transformed into chloralic acids containing C₇ whether the sugar from which they are formed is a hexose or a pentose. In the case of the hexochloraloses one atom of carbon is removed as carbon dioxide. β -glucochloralic acid and xylochloralic acid are identical, and also galactochloralic acid and β -arabinochloralic acid.

Syntheses by means of Mixed Organometallic Derivatives of Zinc. Preparation of Ketonic Acids and Diketones.—E. Blaise and A. Koehler.—To prepare ketonic acids a dibasic acid is transformed into ether acid. This is then converted into ether chloride, which with a mixed organo-metallic derivative of zinc gives a ketonic acid—



If the dichlorides of dibasic acids are used as the starting point the corresponding symmetrical diketones are obtained—



All the diketones the authors have obtained by this method are solid substances of low melting-point, crystallising in petroleum ether.

Preparation of Indazylic Derivatives by means of Orthoketonic Hydrazo Compounds.—P. Carré.—The reduction of *o*-nitrobenzophenone by alcoholic soda and zinc dust gives chiefly orthoaminobenzophenone, a trace of a compound which has indazylic properties being also formed. The production of orthoaminobenzophenone is a fresh instance of the influence of ortho-substituted groups on the alkaline reduction of nitrated derivatives. The reaction is complicated by the partial reduction of the ketonic group to the groups CHOH and CH₂. Orthoazobenzophenone may be prepared by the oxidation of orthoazodiphenylmethane with chromic acid. The reduction of this compound by ammonium sulphide does not give the corresponding hydrazo derivative, but *N*-orthoazobenzophenone-*C*-phenylindazol, which shows that the orthoketonic hydrazo compounds are readily transformed into indazylic derivatives like the orthoaldehydic hydrazo compounds.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 5th inst., the Duke of Northumberland, K.G., President, in the Chair. Mr. L. J. Baker, Mrs. S. G. Brown, and Miss Carvill were elected Members. The Special Thanks of the Members were returned to Dr. Hugo Müller for his donation of £100 to the Fund for the Promotion of Experimental Research at Low Temperatures.

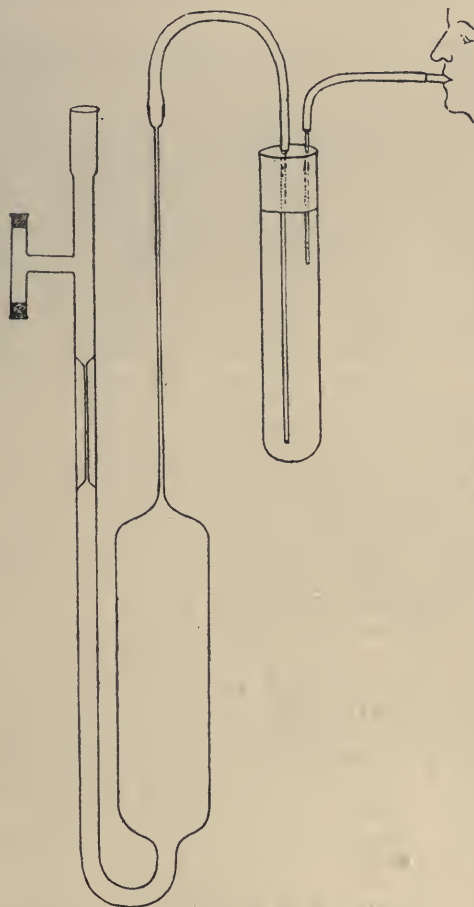
THE CHEMICAL NEWS.

VOL XCIX., No. 2577.

NOTE ON A SIMPLE METHOD FOR FILLING TOLUENE THERMO REGULATORS.

By J. P. McGOWAN, M.A., M.B., B.Sc.,
Bacteriologist to the Royal College of Physicians Laboratory,
Edinburgh; late Ernest Hart Research Scholar.

I HAVE had considerable difficulty and breakages in filling toluene regulators, especially where I was using salt solution as a layer between the mercury and the toluene. I devised the following plan for getting over the difficulties:—A capillary with a slight constriction (to facilitate fusing) near the bulb is drawn from the upper end of the bulb parallel to the limb of the regulator, and equal in length to it. At the upper end of this capillary is an acorn knob to facilitate fitting a rubber tube on. This rubber



tube is taken to a small Woulff's bottle, made with a test-tube, a rubber cork, and two glass tubes. The glass tube nearest the regulator goes to the bottom of the Woulff's bottle, while the other tube goes through the cork only. To fill the regulator, after the side tube has been stopped, suction is made on the rubber tube attached to the short

tube of the Woulff's bottle, and at the same time toluene is poured into the limb of the regulator. This is continued until the whole of the regulator is filled with toluene, and there is a little toluene in the Woulff's bottle. The salt solution is then poured into the regulator limb, and suction made until sufficient salt solution has got round the lower end into the bulb. Mercury is then poured into the limb, and suction again made until enough mercury has got round the lower bend into the bulb. The Woulff's bottle is then detached, and the capillary at the constriction fused in a needle flame of the blowpipe. The limb of the regulator is then filled up with mercury by pouring the mercury into it, placing the bulb of the regulator into fairly hot water, and tapping and joggling the limb at intervals.

I have to thank Dr. Cranston Low for kindly preparing the sketch which accompanies this note.

RECENT RESEARCHES IN RADIO-ACTIVITY.*

By Prof. ERNEST RUTHERFORD, M.A., LL.D., D.Sc., F.R.S.

(Concluded from p. 174).

FROM the radio-active point of view, the α -rays are by far the most important type of radiation emitted by active matter, although their power of penetration is insignificant compared with the β - or γ -rays. They consist of veritable atoms of matter projected at a speed, on an average, of 6000 miles per second. It is the great energy of motion of these swiftly expelled masses that gives rise to the heating effect of radium. In addition, they are responsible for the greater part of the ionisation observed near an uncovered radio-active substance. On account of their importance in radio-active phenomena, I shall devote some little attention to the behaviour of these rays. The work of Bragg and Kleeman, of Adelaide, first gave us a clear idea of the nature of the absorption of these rays by matter. The α particles from a very thin film of any simple kind of radio-active matter are all projected at an identical speed, and lose their power of ionising the gas or of producing phosphorescence or photographic action after they have traversed exactly the same distance, which may conveniently be called the "range" of the α particle. Now every product emits α particles at an identical speed among themselves, but different from every other product. For example, the swiftest α particles from the radium family, viz., that from radium C, travels 7 cm. in air under ordinary conditions before it is stopped, while that from radium itself is projected at a slower speed, travelling only 3.5 cm. We may regard the α particle as a projectile travelling so swiftly that it plunges through every molecule in its path, producing positively and negatively charged ions in the process. On an average, an α particle before its career of violence is stopped breaks up about 100,000 molecules. So great is the kinetic energy of the α projectile that its collisions with matter do not sensibly deflect it, and in this respect it differs markedly from the β particle, which is apparently easily deflected by its passage through matter. At the same time there is undoubted evidence that the direction of motion of some of the α particles is slightly changed by their passage through matter.

The sudden cessation of the ionising power produced by the α -particle after traversing a definite distance of air has been shown by Bragg to be a powerful method of analysis of the number of α -ray products present in a substance. For example, suppose the amount of ionisation in the gas produced by a narrow pencil of α -rays is examined at varying distances from the radium. At a distance of 7 cm. there is a sudden increase in the amount of ionisation, for at this distance the α -particles from radium C enter the testing vessel. There are again sudden changes in the

* A Discourse delivered at the Royal Institution, January 31, 1908.

ionisation at distances of 4.8 cm., 4.3 cm., and 3.5 cm. These are due to the rays from the radium A, the emanation and radium itself respectively entering the testing vessel. The α -ray analysis thus discloses four types of α -rays present in radium in equilibrium—a result in conformity with the more direct analysis. This method allows us to settle at once whether more than one α -ray product is present in a given radio-active material. For example, an analysis by Hahn by this method of the radiation from the active deposit of thorium has disclosed the existence of two α -ray products instead of one as previously supposed. We can consequently gain information on the complexity of radio-active material, even though no chemical methods have been found to separate the products concerned. The range of the α -particle from each product is a definite constant which is characteristic of each product.

The α particle decreases in velocity as it passes through matter. This result is clearly brought out by photographs showing the deflection of a homogeneous pencil of α -rays in a magnetic field before and after passing through an absorbing screen. The greater divergence of the trace of the α -rays on the plate, after passing through the screen, shows that their velocity is reduced, while the sharpness of the band shows that the α particles still move at an identical speed.

In order to make an accurate determination of the constants of the α particles, it is necessary to work with homogeneous rays, and we consequently require to use a thin layer of matter of one kind. For experiments of this character, a wire coated with a thin film of radium C by exposure to the radium emanation is very suitable. The velocity of the α particle and the value e/m , the ratio of the charge carried by the α particle to its mass, can be deduced by observing the deflections of a pencil of α -rays exposed in a magnetic and in an electric field of known strengths. The deflection of a pencil of α -rays in an electric field is small under normal conditions, and special care is needed to determine it with accuracy.

In this way I have calculated the velocity and value of e/m for a number of α -ray products. The velocity of expulsion varies for different products, but is connected by a simple relation with the range of the α particle in air. The value of e/m has been determined for selected products of radium, thorium, and actinium, and in each case the same value has been found. This shows that the α -particles expelled from radio-active substances in general are identical in constitution. They have all the same mass, but differ from one another in the initial velocity of their projection. Although we are sure that the α particles, from whatever source, are identical atoms of matter, we are still unable to settle definitely the true nature of the α particle. The value of e/m found by experiment is nearly 5×10^3 . Now the value of e/m for the hydrogen atom in the electrolysis of water is 10^4 . If the charge carried by the α particle and the hydrogen atom is the same, the mass of the α particle is twice that of the hydrogen atom, *i.e.*, a mass equal to the hydrogen molecule. But we are not certain that they do carry the same charge. Here we are, unfortunately, confronted by a number of possibilities, for the magnitude of m for the α particle is conditioned by the value assumed for e . If the charge of the α particle is assumed to be twice the value of the hydrogen atom, the mass comes out four times the hydrogen atom—the value found for the helium atom. The weight of evidence still supports the view that the α particle is in some way connected with the helium atom. If the α particle is a helium atom with twice the ionic charge, we must regard the helium produced by radio-active bodies as actually the collected α particles the charges of which have been neutralised. This at once offers a reasonable explanation of the production of helium by actinium as well as by radium. In addition, Strutt has recently contributed strong evidence that helium is a product of thorium. Such results are only to be expected on the above view, since the α particle is the only common product of these elements.

The determination of the true character of the α particle

is one of the most pressing unsolved problems in radio-activity, for a number of important consequences follow from its solution. Unfortunately, a direct experimental proof of its true character appears to be very difficult unless a new method of attack is found. We have seen that if the charge carried by the α particle could be experimentally determined, the actual value of m could be determined in terms of the hydrogen atom, since the value of the charge carried by the latter is known. This could be done if we could devise a method of detecting the emission of a single α particle, and thus counting the number of particles expelled from a known quantity of a radio-active substance—for example, from radium. In considering a possible method of attack of this question, the remarkable property of the α particles of producing scintillations in zinc sulphide at once suggests itself. Apart from the difficulty of counting the scintillations, it is very doubtful whether more than a small fraction of the α particles which strike the screen produce the scintillations. Viewed from the electrical side, a simple calculation from the data at our disposal shows that the ionisation produced in a gas by a single α particle should be detectable. The electrometer or electroscope used for measurement would, however, require to be extremely sensitive, and under such conditions it is known that small electrical disturbances are very difficult to avoid.

In order to obtain a reasonably large effect, we require some method of magnifying the ionisation produced by the α particle. In conjunction with Dr. Hans Geiger, I have recently developed a method whereby the electrical effect produced by the α particle can be magnified several thousand times. From the work of Townsend it is known that if a strong electric field acts on gas at low pressure, any ions generated in the gas by an external agency are set in motion by the electric field, and under the proper conditions produce fresh ions by collision with the gas molecules. The negative ion is the most effective ioniser in weak fields, but when the voltage is increased near the point at which a discharge passes, the positive ion also produces fresh ions by collision. In the experimental arrangement the α particle from the active matter is fired through a small opening about 2 mm. in diameter, covered with a thin layer of mica, into a cylinder 60 cm. long and 2.5 cm. in diameter, in which the gas pressure is about 3 cm. of mercury. A thin insulated wire connected to the electrometer is fixed centrally in the cylinder. If the outside cylinder is charged negatively, for a difference of potential of about 1000 volts any ionisation produced in the cylinder is increased about 2000 times by collision. This can be simply illustrated by using the γ rays of radium as a source of ionisation. When a difference of potential is applied to the cylinder, the ionisation produced by the γ rays only causes a slight movement of the electrometer needle. By applying, however, a voltage nearly equal to that required for a discharge through the gas there is a very rapid movement of the needle. On removing the radium there is no appreciable current through the gas. On placing a source of α rays near the small opening in the cylinder so that some of the α particles can be fired along the axis of the cylinder, the electrometer needle does not move uniformly, but with a succession of rapid throws with a considerable interval in between. Each of these throws is due to the discharge produced by a single α particle entering the cylinder, increased several thousand times by the intermediary of the strong electric field. If a sheet of paper which stops the α rays is placed before the opening, the electrometer needle at once comes to rest. The interval of time between the throws is not uniform. This is exactly what we should expect if the number of α particles entering such a small opening is governed by the law of probability. On the average, a certain number of α particles are fired through the opening per minute, but in some cases the interval is less than the average, in others much greater. In fact, by observing the intervals between the entrance of a large number of α particles, we should be able to determine accurately the "probability"

curve of distribution of the α particles with time. For purposes of measurements, the active material, in the form of a thin film covering a small area, is placed in an exhausted tube connected in series with the ionisation cylinder, and at a considerable distance from the hole. The number of α particles entering the opening per minute is counted, and from this the total number expelled can be calculated. Preliminary measurements show that the number of α particles expelled from a known weight of radium is of the same order as the calculated value. When the measurements are completed it should be possible to determine the charge carried by each α particle, since the total charge carried by the α particles from 1 grm. of radium is known. In this way it may be possible to settle whether the α particle is a helium atom or not. In any case, it is a matter of some interest to be able to detect by its electrical effect a single atom of matter, and so to determine directly with a minimum of assumption the magnitude of some of the most important quantities in radio-active phenomena.

ON THE RATE OF EVOLUTION OF GASES FROM HOMOGENEOUS LIQUIDS.*

By V. H. VELEY, F.R.S.

(Concluded from p. 175).

PART II. (with J. C. CAIN, D.Sc.).—THE DECOMPOSITION OF DIAZONIUM SALTS BY WATER.

THIS reaction has been investigated by a number of workers; those who have more particularly studied the kinetics of the reaction are Hausser and Muller, Hantzsch, one of us with Nicoll, Schwalbe, Euler, and Lamplough. It is proposed to discuss certain of these investigations with the view of explaining discrepancies, and of bringing, so far as possible, the conclusions into conformity. The observations detailed below were made, but not published, by the latter, the calculations by the former of us.

All observers are agreed that the reaction, expressible in the simplest form, $\text{RN}_2\text{Cl} + \text{H}_2\text{O} = \text{ROH} + \text{N}_2 + \text{HCl}$, conforms to the monomolecular type, though it might reasonably be supposed that it would belong to the bimolecular type. To explain this matter, the formation of intermediate monomolecular complexes has been assumed (Hantzsch). Though such a hypothesis is probably correct, it has not been utilised generally. On the other hand, observers are not agreed as to (1) storage or detention of nitrogen gas and its amount, or whether the initial delay (so-called induction period) can be attributed solely to this cause, and (2) the effect produced by addition of acid.

1. *Storage of Nitrogen.*—The method adopted for the calculations has been previously described (*Phil. Mag., loc. cit., supra*), and was originally proposed by Esson.

If a portion of the nitrogen gas is detained (while a supersaturated solution is being formed) in continually diminishing quantity z , x is the calculated amount of nitrogen gas after an interval t , and x' the observed amount of nitrogen gas, then $x - x' = z$, or if during a unit interval of time dz is retained while dx is evolved, then dz is a continually diminishing fraction of dx . Throughout natural logarithms are used, and the values of k multiplied by 100 to avoid writing cyphers.

In the following tables the conditions are set forth:—In Column 1 the values of t in minutes; in 2 the values of x calculated, if there were no detention of nitrogen; in 3 the observed values of x' ; in 4 the values of $x - x' = z$, the sum of which gives the total absorption b or Σz ; and in 5 the values of $b - z$.

Series I.

(Ber., 1905, xxxviii., 2513, with added numbers, benzene diazonium chloride).

Conditions:— $a = 58.6$ cc. $k_{10} = 2.92$; total volume of solution = 35 cc.; temperature of reaction = 50°C .

t .	x (calculated).	x' (found).	$x - x'$.	$b - z$ ($b = 2.7$).
1	3.8	—	—	—
2	7.4	—	—	—
3	10.7	9.4	1.3	1.4
4	13.8	13.3	0.5	2.2
5	16.7	16.3	0.4	2.3
6	19.4	19.1	0.3	2.4
7	22.0	21.8	0.2	2.5
8	24.4	24.4	0.0	2.7

Thus after an interval some time between $7'$ and $8'$ the solution is completely saturated with nitrogen gas, and after this point the amount of gas evolved per unit time is the same as that made.

Another method is to solve out for t_1 from the equations—

$$C \times dt = \frac{1}{k} d(x - z) \dots (7),$$

and—

$$C \times dt' = \frac{1}{k} dx \dots (8),$$

then—

$$dt/dt' = d(x - z)/dx = 1 + dz/dx \dots (9),$$

for which Δt = observed time and $\Delta t'$ calculated time are taken for evolution of Δx gas.

In the succeeding table are given in Column 1 the observed times t ; in Column 2 the calculated times t' ; in Column 3 the values of $1 + dz/dx$; in Column 4 the derived value of z per unit volume; and in Column 5 the value of (z) at the end of each interval.

Δt .	$\Delta t'$.	$1 + dz/dx$.	z derived.	$0.31 - z$.
3	2.55	1.18	0.18	0.13
4	3.75	1.07	0.25	0.6
5	4.84	1.03	0.28	0.3
6	5.87	1.02	0.29	0.2
7	6.99	1.01	0.30	0.1
8	8.00	1.00	0.31	0.0

Hence, therefore, at the end of an infinitely small interval of time 0.69 unit of gas is evolved and 0.31 unit retained, at the end of 3' 0.87 unit of gas is evolved and 0.13 retained, at the end of 7' 0.99 unit gas is evolved and 0.01 unit retained. The value of (z) can be calculated from the general expression—

$$z = 0.31(1 - m^{-x}),$$

in which m is a constant to be evaluated from the results.

Logarithmic curves can be drawn taking the values of t for abscissæ and $a - x$ for ordinates from calculated and observed results; when the solution has reached the maximum point of saturation, the course of the two curves is parallel (*cf. curve, mutatis mutandis, Phil Mag., loc. cit.*).

Series II.

(Results unpublished, alluded to as a *blinder Versuch*, *loc. cit., supra*).

Conditions:— $a = 58.1$ cc.; $k_{10} = 2.96$; total volume of solution and temperature as above.

t .	x (calculated).	x' (found).	$x - x'$.	$b - z$ ($b = 3$).
3	10.9	9.2	1.5	1.5
5	16.8	15.9	0.9	2.1
6	19.5	19.0	0.5	2.5
7	22.0	21.9	0.1	2.9
8	24.4	24.4	0.0	3.0

Thus in the first set of observations the total volume of nitrogen retained $b = 2.7$ cc., and in the second = 3.0 cc., values which are within experimental error, which may be

* A Paper read before the Faraday Society, March 2, 1909.

taken as ± 0.05 cc. per 1'; the mean = 2.85 cc. Lamplough (*loc. cit.*, p. 602) describes an experiment (temp. = 62° C.) in which nitrogen gas was evolved from a solution of benzene diazonium chloride at rest, the same condition as above; after an interval of time, not stated, the solution was violently agitated by a rotating paddle, which caused a further evolution of 2.9 cc. to be given off. The coincidence of the two results is, however, rather more remarkable than real; the last value is, doubtless, the difference between the amount of nitrogen gas retained in a supersaturated and that in a normally saturated solution; unfortunately, Lamplough does not give the total volume of his solution, or the total volume of gas which could be manufactured from materials used, hence no exact comparison can be instituted.

Some idea of the degree of supersaturation can be obtained from Cain's results, as interpreted above; from Lord Rayleigh's determination of the density of nitrogen under standard conditions, 2.8 cc. at 50° C. and 760 mm. weigh 3.168 mgrms.; and from the mean of the determinations of Bohr and Bock (*Wied. Ann.*, 1893, xli., 318), and Winkler (*loc. cit.*, *supra*), 35 grms. of water at 50° C. and 760 mm. would dissolve 0.42 mgrm.; hence supersaturation = $3.168/0.42 = 8.4$ approximately. In other words, under the conditions of the experiment (slight variation of pressure being neglected), the amount of nitrogen retained by the solution is 8.4 times the amount which would be dissolved by pure water under the same conditions, a result which appears to be well within the limit of probability. We find ourselves unable to follow the calculations and line of reasoning by which Lamplough arrives at a degree of supersaturation of 100 or more.

It is now proposed to discuss two series out of number given by Hantzsch (*Ber.*, 1900, xxxiii., 2517), which might be cited to prove that the conclusions arrived at above are erroneous.

This writer gives his data in terms of masses of salt, so for the purpose of comparison volumes of nitrogen under standard conditions have been calculated from these masses; this conversion will not, of course, alter the reaction constant K , which affords a check upon the calculations. The methods are as adopted above, but the values of K are multiplied by 1000.

Series III.

(*Loc. cit.*, p. 2530, benzene diazonium chloride).

Conditions:— $a = 200.2$ cc.; $K \cdot 10^3 = 0.64$; total volume of solution = 112 cc.; temperature of reaction = 25° .

t .	x (calculated).	x' (found).	$z = x - x'$.	$b - z (b = 49)$.
60	17.0	8.8	9.2	39.8
87	23.1	14.9	8.2	40.8
139	37.5	27.3	10.2	38.8
175	45.6	36.6	9.0	40.0
200	51.1	43.1	8.0	41.0
226	56.7	51.1	5.6	44.4
341	76.3	77.5	-1.2	49.0

Hence as before, weight of 49 cc. nitrogen gas at 25° C. and 760 mm. = 5.65 mgrms.; weight of nitrogen gas dissolved by 112 cc. water under same conditions = 2.02 mgrms.; supersaturation value in terms of pure water = $5.65/2.02 = 2.8$. In another set of experiments in which the initial delay lasted over 400' the calculated volume of nitrogen gas retained by 85 cc. solution at same temperature = 73.4 cc., and supersaturation value = $8.56/1.53 = 5.6$. Hence, therefore, whether the initial delay lasts 4' or 400', or the volume of nitrogen retained is 2.7 cc. or 73.4 cc., or the temperature of the reaction is 50° C. or 25° C., or volume of solution 35 cc. or 115 cc., the supersaturation value does not exceed the value 8 or thereabouts in terms of pure water as the only available approximation.

Temperature Coefficients.—It might be worth while to point out the uniformity of the temperature factor, if the results at different temperatures by different observers are calculated out by the formula originally proposed by Esson

$k_1/k_2 = (T_1/T_2)^m$ (T = absolute temperature), which, according to general experience from a number of calculations made, gives results more in accordance with observations than that proposed by Arrhenius— $\log (\text{nat.}) k_1/k_2 = m(T_1 - T_2)/T_1 T_2$ (*Zeit. Phys. Chem.*, 1889, iv., 226), which was adopted by Cain and Nicoll (*Journ. Chem. Soc. Trans.*, 1903, 470). The value of m has been calculated from the results of the last named (*Journ. Chem. Soc. Trans.*, 1902, 1434) for diazo salts obtained from various bases, the values of k varying from $k \cdot 10^2 = 0.02$ to $k \cdot 10^3 = 10.9$ (roughly, 1:550), and from Lamplough's results (*loc. cit. supra*) for the diazo salt obtained from aniline.

The results are calculated out in terms of the values obtained at the lowest temperature (taken as correct) as a first approximation; a solution of all the results by the method of least squares would, of course, be more accurate.

Diazo Salt from Aniline.

Cain and Nicoll.		Lamplough.	
T.	m.	T.	m.
293	—	309.0	—
303	42.2	317.3	42.0
313	38.1	324.4	42.4
323	38.2	333.0	41.6
333	42.2	340.0	41.3
Means ..	40.2		41.8

Diazo Salts from Toluidines (Cain and Nicoll).

o toluidine.		p toluidine.	
T.	m.	T.	m.
—	—	303	—
293	—	313	36
303	40	323	38
313	42	333	39
323	41	343	42
Means ..	41		39

Hence, therefore, the value for m for all three salts = 40 within the limits of experimental error; the graph of $\log k_1/k_2$ in terms of $\log T_1/T_2$ is a straight line (*cf.* Harcourt and Esson, *Phil. Trans.*, A, 1895, clxxxvi., 864).

Effect of Addition of Acid.—The question has been raised, as a matter of technical importance, as to whether addition of free acid retards the decomposition of aqueous solutions of diazonium salts. The latter of us (*loc. cit.*, *supra*) showed that the addition of sulphuric acid to the sulphate produced a permanent retardation, the value of $k \cdot 10^2$ being reduced from 3.0 to 2.0 in round figures, and attributed this result to a secondary or dehydrating action. On the other hand, the addition of hydrochloric acid to the chloride or of nitric acid to the nitrate produced no permanent retardation, but it is proposed to show that the addition of acid produces an initial retardation; and that this is not due to increased retention of nitrogen gas is evidenced by the fact that Δx or volumes evolved per unit time do not decrease regularly. The discussion of such a problem presents certain difficulties, as there are two unknown functions—(1) that of nitrogen gas detained, if altered by addition of acid or consequent upon its amount, (2) the lag constant of the acid, which may be the result of one or more complexes, possibly syndiazo compounds (Hantzsch) which yield up their nitrogen less readily. The method of dealing with the problem is identical with that given above, namely, to solve out equations for x in the initial stages from values of t (and of k for final stage), on the assumption that the reaction had proceeded normally from the start, the difference between values of x (calculated) and x' (found) will give a value of z' , which is the resultant of these two causes stated above, namely, nitrogen retention and acid lag. The first hypothesis adopted is that the addition of acid produces no appreciable alteration of the nitrogen gas retained, so that $z' - z$ will represent the lag due to the acid.

Series IV.

(Cain, *loc. cit.*, *supra*, 2515, with added numbers, benzene diazonium chloride).

Conditions:— $a = 60.3$ cc.; $k \cdot 10^3 = 2.93$, 20 mols. HCl; total volume of solution = 35 cc.; temperature, 50°C .

t .	x (calculated).	x^1 (found).	$\frac{z'}{x-x'}$.	z .	$\frac{y}{=x'-z}$.
3	11.0	9.2	1.8	1.3	0.5
5	17.2	16.0	1.2	0.4	0.8
7	22.7	22.0	0.7	0.2	0.5
8	24.7	25.1	0.4	nil	0.4
9	27.4	27.1	0.3	nil	0.3
10	29.5	29.5	nil	nil	nil

The value of b , z , or $\Sigma z' = 4.4$, instead of 2.7 (Series I.), and there is a lag in the first 5', almost constant, and equivalent to 0.5 cc. (value of y), which finally disappears.

Another possible hypothesis is that before observations had commenced a certain volume of nitrogen was at first retained or stored, but just as soon had entered into some stable form of combination. If this value be taken as 2, and all the observed values of x be increased by 2, thereby altering value of $k \cdot 10^3$ from 2.93 to 3.2, then in the equation $\log A/A - (x+2) = (k-k')t$, the lag value $k_1 \cdot 10^3$ in initial stage = 0.1, and the found values (those observed $+2$), and calculated values compare throughout as under:—

Initial Stage, $K^1 \cdot 10^3 = 0.1$

Found.	Calculated.
10.2	11.6
18.0	17.8
24.0	23.6

Final Stage, $K^1 \cdot 10^3 = 0$.

26.7	26.8
29.1	29.2
31.5	31.4
33.7	33.4
35.6	35.3
37.3	37.1
38.9	38.8
40.5	40.2
43.3	43.0
45.5	45.3
47.4	46.8

According to this hypothesis the addition of acid would produce a *permanent accelerating effect* (with initial lag), precisely analogous to that observed in the somewhat similar reaction of the decomposition of ammonium nitrite (*Journ. Chem. Soc., loc. cit., supra*); but to confirm this hypothesis, which might not otherwise be legitimate, it would be necessary to study the effect produced by addition of acid after the initial stage due to detention of nitrogen gas only had passed away. (Another method of dealing with this problem would be to determine the rate of formation of hydrochloric acid with and without previous addition of acid).

Another series of experiments with a further quantity of hydrochloric acid added gave results as under:—

Series V.

($k \cdot 10^3 = 3.01$).

Conditions:— $a = 59.1$ Cl; 60 mols. HCl; total volume of solution = 35 cc.; temperature, 50°C .

t .	x^1 (calculated).	x (found).	$\frac{z^1}{=x^1-x}$.	z .	$\frac{y}{=x^1-z}$.
3	11.1	7.7	3.4	1.3	2.3
4	14.3	11.2	3.1	0.5	2.6
5	17.3	14.8	2.5	0.4	2.1
6	20.1	18.0	2.1	0.3	1.8
7	22.7	21.3	1.4	0.2	1.2
8	25.1	24.2	0.9	0.0	0.9
9	27.4	26.9	0.5	0.0	0.5
10	29.5	29.5	0.0	0.0	0.0

The value of b , or $\Sigma z^1 = 13.9$, instead of 2.7, and it would appear that the initial lag presents two phases, the first

four values of y giving a mean of 2.2, the next two the half value 1.1, and then a disappearance. If the results are calculated out according to the second hypothesis, then the observed values $+2$ are found to be concordant with equation, $\log A/\log A - (x+2) = (k-k')t$, for which $k \cdot 10^3 = 3.3$, $k_1 \cdot 10^3$ for the first phase = 0.5, and for second phase = 0.25, the half value. In like manner the calculated values have been compared with the found values, when a further proportion, namely, 100 mols. hydrochloric acid, were added to the chloride, or 3 mols. nitric acid added to the nitrate. Whichever of the two hypotheses given above is adopted the net result works out the same, namely, under such conditions there are (1) an initial phase with a certain lag, (2) a transition phase with a lag approximately equal to half that of 1, and (3) a final phase in which the lag has disappeared.

Of course, on the general principle *Natura non facit saltum*, phase 1 is not separated from phase 2 nor the latter in its turn from phase 3 by a definite demarcation, but by gradations which might have been rendered more evident if observations had been taken at intervals shorter than one minute. There are, of course, various other points, both technical and theoretical, connected with the above reactions which it is hoped may be dealt with at some future date.

DISCUSSION.

Dr. J. C. CAIN discussed and criticised Mr. Lamplough's experiments on the same subject, particularly with regard to that investigator's measurements of temperature.

Mr. F. E. E. LAMPLOUGH justified his method of determining the temperature of reacting solutions. He criticised the author's calculations on the grounds, among others, that it had been first assumed that the supersaturation was not great enough to affect the values of the velocity constants, and that then these values had been used to prove the absence of any great degree of supersaturation.

Mr. F. E. WESTON described some experiments made by him on the rate of decomposition of a solution of NaNO_2 and NH_4Cl , which had not been published owing to the apparently anomalous results obtained.

Dr. G. SENTER remarked that the fact that solutions became enormously supersaturated was well known, and they were usually well shaken during reaction. Super saturation depended, however, on many complex conditions.

Dr. E. FEILMANN discussed the physical nature of gaseous supersaturation, and suggested that the study of the effect of viscosity on it would have an important bearing.

THE TETRAVALENCY OF OXYGEN.

By J. C. THOMLINSON, B.Sc.

THE article by Mr. Redgrove in the *CHEMICAL NEWS* (1909, xcix., 109) under the above heading, in which the increment of oxygen atoms in a molecule accompanied by a lower molecular heat of combustion than would be expected by theory is advanced in evidence for supporting a quadrivalent view of the valency of oxygen.

The examples given included an increment of carbon atoms with those of oxygen, and as compounds in which the number of carbon atoms increases have a larger experimental error as those carbon atoms increase, might not this lower theoretical heat of combustion be due to experimental error?

I wish also to call attention to the following thermochemical data taken from Roscoe and Schorlemmer's "Chemistry" as indicating some of the difficulties I meet with in dealing with this subject.

The figures from this author are placed in Column I.

I.		II.	
	Cals.	$\text{O}\backslash\text{O}$	Cals.
O_3 ..	-29.378	$3\text{O}=\text{O}=2\text{O}-\text{O}$	-68.000
H_2O ..	-67.940	H_2O ..	-68.360
H_2O_2 ..	-22.927	H_2O_2 ..	-45.300

In Column II. are placed similar data from Pattison Muir's "Thermo-chemistry" as adapted from Thomsen's "Researches" ("Untersuchungen").

In my earliest attempt at the elucidation of thermo-chemical data, I stated that one oxygen atom going to join one already united with one bond to another atom so that the second bond of this atom was united to a valency of the entrant oxygen atom, and the remaining bond of this latter atom of course satisfied was accompanied by an absorption, $\frac{52 \cdot 545}{2} = 26 \cdot 271$ cals., and suggested the figure

$26 \cdot 271 \times 3 = -71 \cdot 813$ cals. as giving the calculated heat of formation of ozone against the experimental value $-68 \cdot 000$ cals. given above.

$O \equiv = -29 \cdot 378$ cals. in Column I. gives $2O \equiv = -58 \cdot 756$ cals., which in some way approximates to the experimental value for the formation of ozone.

I also suggested that $68 \cdot 360 - 26 \cdot 271 = 42 \cdot 089$ cals. is a calculated value for the heat of formation of hydrogen peroxide. The figure at the bottom of Column I. I take to be an error in going to press with the book.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, March 26th, 1909.

Dr. C. CHREE, F.R.S., President, in the Chair.

Mr. F. LLOYD HOPWOOD was elected a Fellow of the Society.

A paper by Dr. J. A. FLEMING and Mr. G. B. DYKE on "*The Production of Steady Electrical Oscillations in Closed Circuits and a Method of Testing Radiotelegraphic Receivers*," was read by the authors.

It was pointed out that at the present time a very large number of oscillation-detectors have been invented for use as receivers in radiotelegraphy; but that there is great difficulty in obtaining quantitative and qualitative tests of these in actual radiotelegraphic stations, partly on account of difficulty of access and partly on account of the varying conditions incidental to practical radiotelegraphic work which are unfavourable to quantitative tests. Availing themselves, however, of the small radiative property of closed circuits, the authors pointed out that by the use of two such nearly closed oscillatory circuits, one being employed as a transmitting station and the other as a receiving station, these being placed at a distance of a few hundred yards from each other, what is practically equivalent to radiotelegraphic stations with open oscillators at very large distances, can be constructed. Methods were then described for producing in one of the closed circuits extremely constant damped oscillations by means of an induction-coil or transformer, a spark-gap on which a steady jet of air is allowed to impinge, and a suitable mercury break. Means were described for ascertaining when the current in this transmitting circuit is constant. The receiving circuit consists of a square circuit of insulated wire which is pivoted in such a manner that it can be turned in any direction, the angular deviations being measurable on scales. This circuit is joined in series with a condenser of variable capacity and with the oscillator-detector to be tested. If the oscillation-detector is of the current-actuated type, it is placed in series with the condenser; if of the potential-actuated type, it is placed across the terminals of the condenser, being associated with a shunted cell and telephone if necessary, or with a telephone simply, if a magnetic detector. It is then possible to set this receiving circuit in such a position that it has no current induced in it by the oscillations in the transmitting circuit; but on turning it through a certain angle, sounds are heard in the telephone indicating the production of oscillations in

the secondary circuit. The angle through which it is to be turned is a measure or indication of the sensibility of the detector. Instances were given of the ease with which detectors of various types, such as a magnetic detector, electrolytic detector, crystal detector, and ionised gas detector, could be compared for relative sensibility. The instrument has been found to be of great use in investigations on ionised gas detectors now being conducted at the Pender Electrical Laboratory. It was also pointed out that such an arrangement permits the effect of various types of oscillations to be investigated, as the transmitting circuit can be made the seat of damped oscillations of various degrees of damping or of undamped oscillations. This method of testing with closed circuits has the advantage that it can be conducted entirely within a large building and by one person. A self-acting apparatus was also exhibited for sending messages or signals by a punched tape.

A paper was also read by Dr. J. A. FLEMING and Mr. H. W. RICHARDSON on the "*Effect of an Air Blast upon the Spark Discharge of a Condenser charged by an Induction Coil or Transformer*."

When an oscillatory discharge of a condenser takes place across the spark-gap in the usual manner by charging the condenser by an induction-coil or transformer, the intermittent spark which takes place is a complex effect. It consists partly of a true condenser discharge and partly of an alternating-current arc due to current coming directly out of the induction-coil or transformer. This arc discharge is a source of difficulty in making accurate quantitative measurements with electrical oscillations, and to produce a uniform oscillatory discharge this true arc discharge must be prevented or arrested. It was shown in the paper that this can be done by a regulated air-blast produced in any convenient manner, thrown upon the spark-gap, provided that the spark-gap is small. As a proof of the advantages to be obtained from this arrangement a number of measurements were given of the decrement and spark-gap resistances of various circuits measured with the Fleming cymometer both with and without the air-blast upon the spark-gap. It was shown that the observations were more regular and the resonance more accurately delineated when the spark-gap was so treated with an air-blast.

The paper also described experiments made to investigate the effect of breaking up the spark-gap into smaller spark-gaps in series, both when the gaps were subjected to an air-blast and also without the air-blast. It was shown, up to a certain length of gap, about 2 mm. in the case of this experiment, that the air-blast had a very decided effect in increasing the mean square value of the discharge current, and also that a similar effect was produced by dividing up the spark-gap into smaller spark-gaps in series provided that the total spark-gap was not increased beyond a certain limit. This increase appears to be due to the suppression of the arc discharge, as shown by the appearance of the image of the spark in a revolving mirror.

With regard to multiple spark-gaps, the general result, however, appears to be that beyond a small limit in length, about 3 mm., nothing is gained by breaking up the spark-gap into spark-gaps in series or by subjecting the spark-gap to an air-blast.

Mr. W. DUDELL congratulated the authors and remarked that the papers contained a great deal of useful material. The use of the earth inductor for testing receivers was a feature of the first paper. He asked Dr. Fleming to what extent the effects obtained in the receiving circuit were due to true radiation, and why they had used coal-gas instead of alcohol in their interrupter. Referring to the authors' method of determining the current in the transmitter, he asked if there was any objection to putting an ammeter in the circuit and reading the current directly. He should also like some more information about the cases in which it was found impossible to obtain a position of the earth inductor giving silence in the telephone. Was it because

the distance apart was not sufficiently great, or was some physical impossibility involved? With regard to the second paper he had always found it possible to get a uniform discharge by using an alternating current of suitable frequency in the primary. He asked the authors if it was the arc or the spark which was blown out by the air and whether the part blown out had a spectrum different from the rest.

Dr. W. H. ECCLES asked how much of the energy absorbed by the receiver was due to radiation and how much to electromagnetic induction. He had obtained results, depending on electromagnetic induction, similar to those described by the authors by using very much smaller apparatus, but he had discontinued his experiments because in practice the whole of the energy received was due to true radiation. He pointed out that a receiver adjusted and tested in a laboratory was never in proper adjustment for actual work. He suggested that the reason it was sometimes impossible to get a position of silence arose from stray radiation falling upon the receiver.

Dr. ERSKINE-MURRAY pointed out that detectors varied greatly in resistance and that therefore a telephone of suitable resistance should be selected in each test.

Dr. A. RUSSELL thought that Prof. Fleming and Mr. Dyke's method of testing radio-telegraphic receivers would be a great help in judging their relative values. He much appreciated the clear distinction drawn between the function of the spark and the arc, as this cleared up some of his difficulties. Although the air-blast of the Lennox blower was doubtless beneficial by preventing arcing, he thought that the fact that the dielectric coefficient of the glass nozzle used was greater than unity might have accelerated the sparking. He mentioned some of the difficulties encountered in computing sparking voltages when there were two gaps in the circuit. In this case it had to be remembered that the sparking voltages at the moment of the discharge are not equal and opposite. When the potentials of the electrodes are known, however, and they are spherical in shape, the sparking voltages with two gaps in series can be calculated with fair accuracy.

Dr. R. S. WILLOWS pointed out that by blowing out the spark the resistance of the path was increased and the rate of charge of energy thereby altered. The fact that greater regularity and greater energy could be obtained could be easily demonstrated by using an electrodeless discharge bulb. Referring to the fact that it was necessary to know the self-induction of one of the circuits, he asked the authors what form of circuit had been chosen and how its self-induction had been calculated. In one of the experiments a resistance r had been added, and he remarked that attention should be directed to its effective resistance under rapidly alternating currents, as this might depend upon whether the added resistance was a pure metal or an alloy.

Mr. L. H. WALTER agreed with Dr. Erskine-Murray that it was necessary to choose a suitable telephone when making a test. Although the electrolytic detector was supposed to be more sensitive than the magnetic form, it was possible to choose a telephone of such a resistance as to make the magnetic detector appear the more sensitive.

Dr. FLEMING, in reply, said that it was impossible to state precisely what proportion of the current produced in the receiving circuit was due to true radiation from the closed transmitting circuit, and how much was due to electromagnetic radiation, but from his point of view it did not matter. All that was necessary was that a feeble oscillatory current should be produced in the receiving circuit which should be capable of being varied by turning the receiving circuit through a certain angle, and whether this was due to actual detachment of energy from the transmitting circuit, or to the mere movement of lines of magnetic force backwards and forwards through space, seemed immaterial. The oscillation detector in any case is a mere detector of oscillations.

In reply to Mr. Duddell, he said that there was no objection to putting an ammeter in the transmitting circuit

provided it was a low resistance instrument and did not produce any sensible damping of the oscillations.

As regards the existence of an exact zero point, this seemed to be a question of distance from the transmitter. It had been usual at University College to work with two coils about 60 feet apart, and at that distance some very sensitive oscillation valves detected sounds which might be due to the action directly upon the valve or upon the connecting wires, but by going to larger distance, it was possible to get complete silence at the telephone.

With respect to the use of coal-gas or alcohol in the interrupter, coal-gas had proved itself to be incontestably superior to alcohol.

As regards the action of the air-blast, it appears tolerably certain that the part of the discharge which is blown away is that due to energy coming directly out of the induction-coil or transformer.

In reply to the remarks of Dr. Eccles, he said that they had found it necessary to work at a certain distance from the transmitter, but that when this was done the order of sensitiveness in which oscillation-detectors were arranged by the apparatus shown was also the order in which they were found to be sensitive when employed in actual radio-telegraphic work. It is necessary not to work the transmitter and receiver too near to one another, otherwise there are direct effects on wire connections, rheostats, &c., which obscure the real effects.

In reply to Dr. Willows, Dr. Fleming said that the reason for choosing the rectangular form of circuit was because the inductance could be readily calculated from formulæ given in well-known text-books.

With respect to the remarks of Mr. Walter and Dr. Erskine Murray, Dr. Fleming agreed that it was necessary to choose a telephone of suitable resistance, and that the results taken with different telephones would not be the same.

Dr. S. W. J. SMITH read a paper "*On the Action between Metals and Acids and the Conditions under which Mercury causes Evolution of Hydrogen.*"

The action between an acid and a metal, which results in the replacement of hydrogen, can be formulated without the aid of any hypothesis beyond the assumption that it is approximately reversible. The mode of formulation suggests a kinetic picture of the process by which equilibrium is in certain cases attained. This was described by the author, and it was pointed out that if a steady state is reached, after a certain quantity of hydrogen has been evolved, it will be defined by an equation of the form $ahM = bmH$. In this, a and b are constants at a given temperature, h and m are the concentrations of the hydrogen ions and of the metal ions respectively in solution, and H and M are specific constants of hydrogen and of the metal.

The experiments described in the paper may be regarded as an attempt to justify the above equation when the metal is mercury. It is shown that hydrogen can be made to appear after equilibrium has been reached, either by reducing the value of m or by increasing the value of h .

The effects produced by HCl and H_2SO_4 are nearly alike (except for secondary effects with concentrated sulphuric acid), and it is probable that other acids would act in the same way.

It would therefore appear to be justified for this case at least that the action between metals and acids can be formulated in a purely physical way.

Referring to the action with concentrated sulphuric acid, the author described and explained how sulphuretted hydrogen only, or mixtures of sulphuretted hydrogen and hydrogen, could be obtained at will by varying the rate of removal of the mercury salt from the solution in contact with the metal.

Dr. W. WATSON congratulated the author and remarked that in physical chemistry hypotheses were often used which were not based on experimental evidence. Dr. Smith had shown that his hypothesis corresponded with

actual physical facts, and his theory could be looked upon with satisfaction.

In reply to a question by Mr. F. E. SMITH, the author explained that the process by which the concentration of the mercury salt in solution was reduced below the amount necessary to prevent evolution of hydrogen was endothermic.

FARADAY SOCIETY.

Ordinary Meeting, March 30th, 1909.

Dr. H. BORN in the Chair.

THE following nominations for the Officers and Council (1909-10) to be elected at the Annual General Meeting were announced:—

President—J. Swinburne, F.R.S., M.Inst.C.E.

Vice-Presidents—G. T. Beilby, F.R.S.; Sir R. A. Hadfield, F.R.S.; Prof. A. K. Huntington; Dr. Ludwig Mond, F.R.S.; Lord Rayleigh, O.M., F.R.S.; Prof. A. Schuster, F.R.S.; Ernest Solvay.

Treasurer—Dr. F. Mollwo Perkin.

Council—E. J. Bevan, F.I.C.; Bertram Blount, F.I.C.; A. C. Claudet, M.I.M.M.; W. R. Cooper, M.A., B.Sc.; S. Z. de Ferranti, M.I.E.E.; F. W. Harbord, F.I.C.; W. Murray Morrison, M.Inst.C.E.; H. F. K. Picard, M.I.M.M.; J. L. F. Vogel, M.I.E.E.; N. T. M. Wilshire, D.Sc.

A paper by Messrs. E. SABERSKY and E. ADLER on "A New Electrical Hardening Furnace," was read by Mr. Adler. The reading of the paper was illustrated by lantern slides.

The authors described a new electrical hardening furnace built by the Allgemeine Elektrizitäts-Gesellschaft, Berlin, and consisting of a fire-clay crucible containing a bath of metallic salts. By means of the electric current these salts are melted and kept at a temperature which can be made to reach any value up to, say, 1400° C. For working this furnace alternating current of a voltage not exceeding 70 is used, and by means of a transformer fitted with regulator and switchboard, the supply voltage is lowered to this value.

The authors also explicitly described the method of operating the furnace and of measuring its temperature.

They also further set forth the general principles underlying the hardening process, and used for demonstrating these the diagram of solidification-points originally developed by Sir William Roberts-Austen. They showed that hardening means, essentially, the fixation of the "martensitic" state of the steel.

The hardening process consists of—

- (a) Heating up of the steel to a temperature above the transition line.
- (b) A subsequent rapid cooling down.

The authors gave a list of propositions covering the features an ideal furnace should possess, and tried to show that the new electrical furnace fulfils these conditions to a greater extent than any furnace on the market. They also claim that the operating cost of the new electrical furnace on the basis of equal output works out lower than that of gas-fired muffle or bath furnaces.

Mr. F. W. HARBORD (communicated) described some of his experiences with the furnace in heating a large number of steel bars from 800° C. to 1230° C., and keeping them at a high and fairly constant temperature for some time; this he was able to do without difficulty. If a furnace could be designed to compete with present large heating furnaces, its possibilities should be very great.

Mr. W. ROSENHAIN (communicated) thought the furnace had decided advantages for the hardening and tempering of tool steels. He thought some care would be required in the selection of the fused salts; nitrates, for example, would have an oxidising effect on steel. Too rapid heating of a piece of metal of uneven cross-section might be unde-

sirable, as expansion stresses would be set up. The uniformity of temperature attained was probably largely due to lagging. He hoped that use of the furnace would throw light on such questions as whether heating to what are excessive temperatures when the metal is exposed to furnace atmospheres is also injurious when the metal is submerged in fused salts.

Mr. C. R. DARLING (communicated) criticised the authors' figures for costs of working. In works in which producer gas was available for the gas furnace, the financial superiority of the electric furnace would disappear. He suggested the use of an optical pyrometer for temperatures above 1100° C.

Mr. T. VAUGHAN HUGHES (communicated) considered that the electric furnace had many drawbacks compared with producer gas-fired equipments, such as too sudden heating, the trouble in dealing with fused salts, and the difficulties of handling large quantities of goods. He was of opinion, too, that its efficiency was low compared with existing furnaces, especially for maintaining comparatively low temperatures. He added some particulars of such gas-heated furnaces, which, he stated, easily realise the advantages claimed for the electric furnace, which, excepting for very precise and scientific investigations, could not compete with a properly designed producer gas-fired furnace.

Mr. W. C. PREBBLE remarked on the danger of suddenly heating complicated tools.

Dr. J. A. HARKER thought that the amount of energy consumed in the furnace could be greatly reduced by improved lagging. The method of heating up the bath initially with a carbon rod seemed liable to difficulties. Had fused fluoride salts been actually used?

Dr. C. H. DESCH considered that the furnace did away with the old difficulty of judging hardening by means of skill acquired with the eye. A pyrometer was of no use in an ordinary muffle.

Mr. C. WEISS said the authors had somewhat penalised gas in their estimates of cost.

The CHAIRMAN said the amount of electrolysis would depend on the form of the current-wave. It might be advantageous in some cases.

Mr. E. ADLER replied to the various points raised. The rate of heating depended on the voltage, and was under control. No action of the fused salts on steel had been observed. Mr. Hughes admitted the scientific value of the furnace, but appeared to consider that scientific accuracy was unnecessary for scientific work. Of course much larger furnaces than those now made could be built, and their efficiencies would increase accordingly. Optical pyrometers might perhaps be used above 1400° C.; for ordinary purposes thermo-couples were preferable. There was no difficulty in starting the furnace, which took some fifteen to twenty minutes. Fluoride salts had only been used experimentally.

A paper entitled "The Relation between Composition and Conductivity in Solutions of Meta- and Ortho-phosphoric Acids," by Dr. E. B. R. PRIDEAUX, was read in abstract by Dr. T. M. LOWRY. (Already inserted).

Mr. F. MOLLWO PERKIN read a paper on "The Electro-analysis of Mercury Compounds with a Gold Cathode."

The results obtained were always slightly high—from 0.5 to 1 per cent. This was at first attributed to occluded hydrogen; but it was not found that the gold electrode increased in weight when made the cathode in dilute sulphuric acid, and the current passed for six to twenty hours. When the electrode coated with mercury was treated in a similar manner, it also showed no increase in weight. The increase in weight could hardly be due to oxidation since the electrode was cathode, and when a platinum electrode was run in series with it the mercury deposited upon the platinum was always slightly less than was theoretically required. The author was consequently unable to account for the results, but pointed out that a gold electrode could not be satisfactorily used for analytical purposes.

A rotating silver electrode showed similar results—viz., the weight of mercury was too high. Usually the time required to deposit the mercury was from five to six hours, but by placing the cell and electrodes in a powerful magnetic field in such a way that the liquid was caused to swirl, the mercury was deposited in about fifty minutes. The results in this case, however, were also too high.

The author also described two new quartz vessels which he had devised for depositing mercury or other metals upon a mercury cathode, one of them being fitted with a syphon side tube.

In conclusion, the author said that undoubtedly the best electrode for depositing mercury upon was one of mercury, and that the deposition was extremely rapid if a rotating anode was employed.

RÖNTGEN SOCIETY.

THE collection of early tubes and other X-ray apparatus, which the Röntgen Society has been gathering together, having been completed and lodged in the Victoria and Albert Museum, Mr. J. H. GARDINER, editor of the Society's *Journal*, took occasion at the meeting on April 1st to read a paper reviewing the evolution of the X-ray tube. He said that he had been greatly impressed, in making his researches for this purpose, by the fact that in almost every instance in which an advance had been made, the seed from which the advance sprang was to be found in the work of Sir William Crookes. Indeed, so close had been the association of Crookes with the modern X-ray tube and its forerunners that it was one of the most extraordinary things in modern science that Crookes did not discover the rays when making his investigations in 1874, instead of leaving them to be discovered by Röntgen twenty-one years later. There appeared, however, to be a psychological moment for great discoveries, and similar examples of the "little more, and how much it is" had often occurred in physics. Speaking of the most recent developments in tube manufacture, he characterised the introduction of tantalum as the one of greatest promise. He thought the tube of the future would be a smaller and simpler device than the ones at present on the market, which were often good examples of glass-blowing rather than convenient instruments for the use of the physicist or the medical man. He brought forward a very simple suggestion for prolonging the life of X-ray tubes. His plan was to use a small magnet at the end of the tube, so as to deflect the cathode rays on to another part of the target (in this case of tantalum) when the first part had become worn.

In the subsequent discussion Mr. W. DUDELL thought that this magnetic deflection would be of no use except with tantalum, and that it was only in connection with the more modern tubes that it could be properly applied.

Mr. CAMPBELL SWINTON thought that such a procedure, although simple and ingenious, would make a difference to the results in point of sharpness. Owing to the fact that the cathode rays were not homogeneous but were of varying velocities, when the focus was deflected a proper focus was not regained, and the result would be a fuzzy image or possibly a series of images. Mr. Swinton thought that tantalum cathode for X-ray tubes might be of considerable value. In some experiments he had been carrying out with great powers—passing more than 50 milliampères through the tube on occasion—one of his chief difficulties arose from the tendency of the cathodes to melt. Aluminium quickly became red-hot, while the melting-point of magnesium was about the same, and with platinum they got a deposit all over the glass. If the cathodes could be made of tantalum its higher melting-point would be a great advantage.

Mr. F. H. GLEW thought that tantalum cathodes would settle the point as to whether the cathode itself was a source of X-rays due to recoil. It seemed possible that X-rays, at any rate of low penetrating power, might be

produced at the cathode, but if so the effect was masked by the comparative inefficiency of aluminium as a target, and therefore as a source of X-rays.

NOTICES OF BOOKS.

Rapid Methods for the Chemical Analysis of Special Steels, Steel-making Alloys, and Graphite. By CHARLES MORRIS JOHNSON. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1909.

FULL experimental details of methods of rapidly determining the composition of steels and alloys are given in this book. Many of the processes described have been worked out or modified by the author, who in addition has devised many ingenious adaptations of apparatus for special purposes. The user of the book cannot fail to be impressed by the intimate knowledge displayed in it of the minutiae of steel analysis, and he will have every reason to feel perfect confidence in the author's directions, even when they are opposed to those generally found in books on the subject. One of the most interesting methods described is the determination of phosphorus in ferro-vanadium. The results obtained by the usual methods are notoriously unreliable, while the author's aluminate process has proved quite accurate when applied to specimens containing known amounts of phosphorus. There are many other new suggestions in the book, which is a valuable addition to the literature dealing with steels and their analysis.

Laboratoriumsbuch für Tinktorial-chemiker, Koloristen, Ingenieure und Technische Reisende. ("Laboratory Book for Tinctorial Chemists, Colourists, Engineers, and Technical Travellers"). By Dr. FRANZ ERBAN. Halle-a-S.: Wilhelm Knapp. 1908.

THIS is a difficult subject to treat in one short volume, and it may be doubted whether the author has been very happy in his decisions as to what to discuss and what to omit. The young chemist who aims at specialising in the colour industries would now-a-days begin to fit himself for his career by attending technical classes, where he would undoubtedly work thoroughly through much of the laboratory work which is described cursorily in the book. The necessary knowledge of machinery and apparatus can hardly be satisfactorily obtained from books, and although notes on the technical commercial traveller's duties might conceivably be useful, they are necessarily so general that it is very difficult to glean any definite information from them.

Histoire du Développement de la Chimie depuis Lavoisier jusqu'à nos Jours. ("History of the Development of Chemistry from Lavoisier to the Present Time"). By A. LADENBURG. Translated from the Fourth German Edition. By A. CORVISY. Paris: A. Hermann and Fils. 1909.

ALTHOUGH this history of chemistry is comparatively brief, so that it is unavoidable that the growth of some branches of the science should be left almost entirely unchronicled, it is written in a bright and interesting style, and the student will find it easy to gather from it a good general idea of the development of present day theories. As regards the history of organic chemistry it is fairly full, and the state of the science in the middle of the last century is made very clear. The translation has been made from the fourth German edition, to which a chapter was added dealing with the discovery and investigation of the radio-active elements, the developments of the theory of valency, the chemistry of the colloids, and other subjects in which special progress has been made since the beginning of the present century.

Untersuchungen über Kohlenhydrate und Fermente (1884—1908). ("Researches on Carbohydrates and Ferments"). By EMIL FISCHER. Berlin: Julius Springer. 1909.

THE size of this book, which comprises nearly 900 pages, is a striking witness to the author's prodigious activity in the investigation of the carbohydrates and ferments. It contains all the articles which have been published by Prof. Fischer during the last twenty-four years, together with the lectures and addresses he has delivered on the subject. In addition some articles written by his pupils, in which researches performed under his direction are described, are also included. In most cases the papers are reproduced word for word from the originals, some few explanatory notes having been added. One article on synthesis in the sugar group has been specially written for the book in order to bring it down to date. The arrangement is as systematic as possible, the papers being classified under the headings Nitrogen Derivatives of Sugars, Mono- and Di-Saccharides, Glucosides, and Ferments, while in the general part summaries are given of the chemistry of the sugar group and of the carbohydrates and their importance in physiology.

Analyse und Konstitutionsermittlung Organischer Verbindungen. ("Analysis and Determination of the Constitution of Organic Compounds"). By Dr. HANS MEYER. Second Edition. Berlin: Julius Springer. 1909.

THE applications of analytical processes to organic compounds, including elementary analysis and the determination of physical constants, is exhaustively treated in this book. Detailed descriptions, with illustrations, of apparatus for all purposes are provided, and notes are added on the special advantages of different methods under various conditions. The second edition contains a fuller account of methods of ascertaining the constitution of a substance by studying the products obtained by oxidation, reduction and fusion with alkalis, and quantitative estimations of groups of atoms are also described in detail, groups containing sulphur being included for the first time. The book is of a most thorough and comprehensive nature, and should prove invaluable as a work of reference, especially for chemists engaged in organic research work.

CORRESPONDENCE.

THE INSTITUTE OF CHEMISTRY AND RESEARCH WORK.

To the Editor of the Chemical News.

SIR,—Professor Kipping pointed out a serious defect in the Institute of Chemistry, and Professor Frankland apparently objects to the criticism. It will not do the Institute any good to attempt to prevent fair criticism of its work.

The Charter was granted for definite purposes; admission to the F.I.C. after technical research was undoubtedly intended as a ground for admission as well as by examination.

Professor Frankland's address and letter appear to contradict one another. In the address, he asks—Should not these chemists have been admitted to the Institute?—presumably without examination. In his letter, he asks how the Institute can tell if such chemists ought to be admitted. I believe that when the Institute started many such chemists were admitted.

In addition to the already overloaded three years' training, it is now proposed to require a working knowledge of French and German in the Final. Has the training of the Institute in technical chemistry been drawn up after consultation with the leading chemical and

metallurgical manufacturers? I presume that those who employ technical chemists know best what they require.

Some years ago I was a student of the Institute, but I gave up their training, although Dr. Frankland strongly advised me to continue it; I can assure him I have never had any cause to regret severing my connection with the Institute.

The Institute does not cater for a large number of students who go in for technical work. There are large numbers of chemists who have had no college training whose qualifications are as good as any F.I.C. or D.Sc. A five years' training in evening classes, while holding a junior position in a technical laboratory, is very often a better training than three years at college.

The fees of the Institute are far too high for many who have to earn their living by chemistry.—I am, &c.,

ERNEST A. LEWIS.

310, Dudley Road, Birmingham,
April 10, 1909.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlviii., No. 9, March 1, 1909.

Equilibria between Solid and Liquid Phases in the Mixture $\text{NaCl} + \text{H}_2\text{O}$.—Camille Matignon.—The results obtained by different investigators for the fusion curve of the binary system water and rock-salt do not agree well. The author finds that the concentration of the eutectic mixture is 30.7, which is very nearly that obtained by de Coppet. The amount of salt to be added to snow in order to melt it increases as the temperature is lowered, and below -21.3° there is no stable mixture of salt and snow which remains liquid. If calcium chloride is substituted for sodium chloride, snow at a temperature of -55° can be melted.

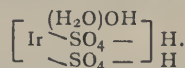
Action of Hydrochloric Acid Gas on Amorphous Silicon.—A. Besson and L. Fournier.—Hydrochloric acid reacts with amorphous silicon at a relatively low temperature. From the products of the reaction the authors have isolated two liquids, the one distilling below 0° (at about -10°) and corresponding to the formula SiH_3Cl , and the other distilling at about 12° , and having the composition SiH_2Cl_2 . They are both very mobile, and are decomposed by water and alkalis, setting free hydrogen. SiH_3Cl can be prepared by acting on the chloride SiCl_4 with calcium hydride.

Ammoniacal Iridodisulphates.—Marcel Delépine.—The action of boiling sulphuric acid on a chloroiridate or chloroiridite in presence of ammonium sulphate yields three ammonium salts. The first, $\text{HO}(\text{H}_2\text{O})\text{Ir}(\text{SO}_4)_2 \cdot (\text{NH}_4)_{0.5}\text{H}_{1.5}$, is dark green and dissociates into the second in water according to the equation—

$3[\text{A}](\text{NH}_4)_{0.5}\text{H}_{1.5} \rightleftharpoons [\text{A}](\text{NH}_4)_{1.5}\text{H}_{0.5} + 2[\text{A}]\text{H}_2$, where A represents the complex $\text{HO}(\text{H}_2\text{O})\text{Ir}(\text{SO}_4)_2$. This second salt is interesting because its formula, written in the usual way for double salts, would be—

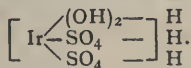


and instead of being a basic salt it is one in which the ammonia is at least as firmly bound as in ammonium sulphate. To explain this it is simplest to regard iridosulphuric acid as a dibasic acid of formula—



When an excess of ammonia is added to a green solution a dark brown coloration is produced, and on the addition

of alcohol a precipitate of formula $\text{Ir}(\text{OH})_2(\text{SO}_4)_2(\text{NH}_4)_3\text{H}_3$ is obtained. This may be regarded as a salt of the tribasic acid—

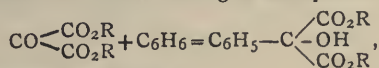


All these formulæ conform to Werner's rules if SO_4 is given two co-ordination places.

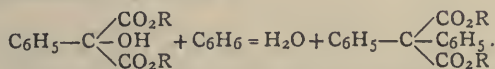
Action of Carbon Monoxide on Chromium, Nickel, Manganese, their Oxides and Alloys.—Georges Charpy.—A current of carbon monoxide was passed over the above metals, or their oxides heated in an electric furnace, and the amount of carbon dioxide in the gas and the variations in the weight of the metal or oxide were determined. With nickel at 1000° there is practically no reaction. Nickel oxide is completely reduced to the metallic state. Manganese and rich ferro-manganeses absorb carbon monoxide at 1000° , and finally set it free again without giving any carbon dioxide; the manganese is converted into monoxide and carbon is deposited. Mn_3O_4 is reduced to the monoxide, and carbon monoxide has no action on the latter oxide. Chromium behaves like manganese except that the sesquioxide is not reduced. Steels containing chromium or manganese behave as if the two metals were simply in juxtaposition.

Researches on Occluded Gases contained in some Common Metals.—B. Delachanal.—With aluminium, magnesium, zinc, tin, and platinum the occluded gases are found to be carbon monoxide, hydrogen, and nitrogen. Methane appears to be formed by the action of hydrogen upon carbon monoxide, but it is not strictly speaking occluded.

Condensation of Mesoxalic Ethers with Aromatic Carbides.—A. Guyot and G. Esteva.—Mesoxalic acid can condense with toluene in presence of concentrated sulphuric acid. This condensation is a particular case of a general reaction, and all aromatic hydrocarbons undergo analogous condensations. Using mesoxalic ethers instead of the free acid two principal fractions are obtained. The first fraction is formed according to the equation—



and the second as follows :—



The authors have thus prepared various condensation products such as methyl phenyl tartronate.

Elaterine and some of its Derivatives.—A. Berg.—Acetic anhydride reacts readily with elaterine, giving a diacetyl derivative of formula $\text{C}_{32}\text{H}_{42}\text{O}_9$. Molecular weight determinations give 565 and 575 instead of 570, which would agree with the author's proposed formula $\text{C}_{28}\text{H}_{38}\text{O}_7$ for elaterine. Hemmelmayr's formula would give 502. With alcoholic potash elaterine condenses, giving up one molecule of acetic acid, the reaction being— $\text{C}_{28}\text{H}_{38}\text{O}_7 + \text{H}_2\text{O} = \text{C}_2\text{H}_4\text{O}_2 + \text{C}_{26}\text{H}_{36}\text{O}_6$. Molecular weight determinations again agree well with the author's formula. The same applies to anhydroelateridine. The bromine derivatives cannot be used for finding the formula, for they cannot be obtained in a pure state.

Action of Semicarbazide on Chlorinated Aldehydes.—André Kling.—Chloral gives an unstable compound, $\text{C}_3\text{H}_6\text{O}_2\text{N}_3\text{Cl}_3$, with semicarbazide. Under the action of warm water it yields semicarbazone glyoxylic acid. A semicarbazone of dichloraldehyde, $\text{C}_3\text{H}_5\text{OCl}_2\text{N}_3$, is prepared by evaporating an alcoholic solution of semicarbazide with dichloraldehyde hydrate. When suspended in water and boiled it gives the semicarbazone of glyoxal. Monochloraldehyde gives a product of formula $\text{CHCl}_2\text{CH}=\text{N}\text{---}\text{NH}\text{CO}\text{NH}_2$.

Sensitive Reactions for the Identification of Glycerin.—Georges Denigès.—Glycerin gives a blue-green coloration with codéin, blood-red with resorcin, emerald-green with β -naphthol, and wine-red with thymol. In presence of potassium bromide a violet-red coloration is obtained with salicylic acid, and dark blue with guaiacol. With phenylhydrazine and sodium acetate it gives a yellow precipitate of glycerosazone, and the osazone of methylglyoxal in presence of sulphuric acid. Glycerin gives a black precipitate of mercury with Nessler's reagent, red cuprous oxide with Fehling's solution, and white cuprous ferrocyanide with Fehling's solution and ferrocyanide.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlii., No. 3, 1909.

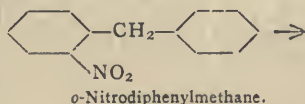
Freezing-out of Jellies.—G. Bruni.—In order to ascertain the difference between reversible and irreversible colloids as regards their behaviour on cooling, fish glue was chosen as a type of the former, and silicic acid of the latter. Both of them were carefully purified and dialysed. The jellies obtained were cooled to -20° for several hours, and in subsequent experiments the temperature employed was -80° . On examining the masses which had frozen out no apparent difference between them was detected; in both cases the ice crystals and the particles of colloid could be recognised. But when the two preparations were gradually warmed it was found that with fish glue the frozen out mass gradually changed into the jelly without apparently melting, while the silicic acid preparation yielded small hard leaflets which looked almost crystalline but were found under the microscope to be amorphous. These were filtered off, dried between blotting-paper, and the water in them determined. It was found that they consisted of a hydrated silicic acid; their composition varied between $\text{SiO}_2 + 0.788\text{H}_2\text{O}$ and $\text{SiO}_2 + 3.67\text{H}_2\text{O}$.

Light Reactions of White and Yellow Diphenyloctatetrene.—Hans Stobbe.—In presence of oxygen both white and yellow diphenyloctatetrene are sensitive to light, the products being benzaldehyde or benzoic acid. The white variety is not converted into the yellow variety. In absence of oxygen only the one hydrocarbon is sensitive to light; it undergoes a photo-isomerisation as follows :—

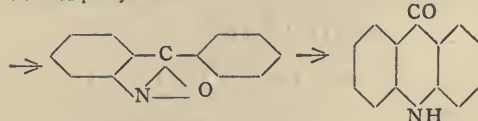
Yellow diphenyloctatetrene $\rightarrow$ White diphenyloctatetrene.
M. p. 225° . M. p. 124° .

This process is analogous to the transformation of isostilbene into stilbene, and the diphenylbutadienes cis-cis and cis-trans into the third stereoisomer trans-trans. While, however, the stilbene and diphenylbutadiene with one and two unsaturated carbons respectively can be isolated, diphenyloctatetrene with four unsaturated carbons can only be isolated in absence of air owing to the readiness with which it undergoes photo-oxidation.

New Method of making Acridone.—A. Kliegl.—When o-nitrodiphenylmethane is heated to 300° water vapour is evolved and a crystalline residue is left. This residue on distillation yields some o-amido-benzophenone and acridone. Probably phenylanthroxan is formed as an intermediate product, and the reaction may be represented as follows :—



o-Nitrodiphenylmethane.



Phenylanthroxan.

Acridone.

New Method of Preparing Pyridazine.—S. Gabriel. —Ketoglutaric acid evaporated to dryness on the water-bath with hydrazine sulphate and caustic soda solution yields pyridazinone-3-carboxylic acid, from which pyridazine-3-carboxylic acid is obtained by treatment with bromine. The last acid gives pyridazine quantitatively on fusing, and this can be converted into chlorpyridazine by warming with phosphorus oxychloride. The chlor-compound is converted into pyridazine by the action of phosphorus and hydriodic acid.

MISCELLANEOUS.

Royal Institution.—On Tuesday next, April 20, at 3 o'clock, Prof. F. W. Mott begins a course of two lectures on "The Brain in relation to Righthandedness and Speech"; and on Thursday, April 22, Mr. James Paterson delivers a lecture on "How a True Art Instinct may be best Developed," being the first of three lectures on "Aspects of Applied Aesthetics"; on Saturday, April 24, Mr. R. T. Günther begins a course of two lectures on "The Earth Movements of the Italian Coast and their Effects." The Friday Evening Discourse on April 23 will be delivered by Mr. Alexander Siemens, on "Tantalum and its Industrial Applications"; and on April 30 by Dr. Edmund Gosse, on "Pitfalls of Biography."

Colour Reactions of Indolic Substances with Sugars.—Julius Gnezda.—With α -methylindol an aqueous solution of glucose gives a green coloration in presence of hydrochloric acid. The author has further experimented with various sugars and has found that all those which possess the group $-\text{CHO}$ (or a ketonic group which is transformed into CHO by the addition of alkalis) give the reaction. The $-\text{CHO}$ group reacts with the methinic $\equiv\text{CH}$ of two molecules of α -methylindol. Free formaldehyde does not give the reaction. Moreover, two sugars such as glucose and arabinose may behave differently when heated. Hence the reaction is not due to the $-\text{CHO}$ group only, nor to the co-existence of this group with the terminal CH_2OH , which is the same in glucose and arabinose.—*Comptes Rendus*, cxlviii., No. 8.

NOTES AND QUERIES.

*. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Sea-water for Boilers.—Will any reader be good enough to inform me—

1. Will sea-water whilst being evaporated at a temperature of about 307°F . give off hydrochloric acid, HCl ? Evaporated steam, after being condensed, to be used as boiler feed-water.
2. If HCl is not generated at this temperature, will the salts in solution (hydrogen and chlorine) be carried over in the vapour, and the acid generated in the boiler when the temperature is about 370 – 375°F .?
3. Will the acid (HCl) remain in the boiler water at a temperature of 370 – 375°F ., or will it be discharged into the vapour space and mix with the steam?
4. Will the acid, if generated, be of sufficient strength to corrode Muntz metal tubes of the condenser—tubes 1.5 copper, 1 zinc?

These questions apply to marine boilers using fresh water when starting the voyage, loss being made up from evaporators. Leaky condensers are getting very common, and I take it that this corrosive acid is at work in a dilute state all the time, so that it is only a matter of time till the condenser tubes get eaten through.—CORROSION.

MEETINGS FOR THE WEEK.

TUESDAY, 20th.—Royal Society of Arts, 4.30. "South Africa," by Hon. Charles G. Murray.
Royal Institution, 3. "The Brain in relation to Right-handedness and Speech," by Prof. F. W. Mott.

WEDNESDAY, 21st.—Microscopical, 8. "Recent and Fossil Foraminifera of the Shore Sands of Selsea Bill, Sussex," by E. Heron-Allen. "Disappearance of the Nucleolus in Mitosis," by E. J. Sheppard.

THURSDAY, 22nd.—Royal Institution, 3. "Aspects of Applied Aesthetics," by James Paterson, A.R.S.A.

FRIDAY, 23rd.—Royal Institution, 9. "Tantalum and its Industrial Applications," by Alexander Siemens.

Physical, 5. "Want of Symmetry shown by Secondary X-rays," by W. H. Bragg and J. L. Glasson. "Transformations of X-rays," by C. A. Sadler. "Theory of the Alternate Current Generator," by T. R. Lyle.

SATURDAY, 24th.—Royal Institution, 3. "The Earth Movements of the Italian Coast, and their Effects," by Robert T. Günther.

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THE CHEMICAL NEWS.

VOL XCIX., No. 2578.

THE DISCOVERY OF IODINE.

By F. D. CHATTAWAY, F.R.S.

ALTHOUGH the elementary nature of iodine has never been questioned, the substance has, ever since its discovery, attracted an unusual amount of attention. This is not surprising if one considers its metallic appearance, the remarkable colour of its vapour, the explosive compound which it forms with ammonia, and the beautiful blue compound it yields with starch. It has found extensive employment in medicine, photography, and in volumetric analysis. Its anomalous position with regard to tellurium in the periodic table even to-day arouses interest.

It is somewhat remarkable that iodine should have remained unknown till the year 1812, in view of the fact that it is present in many substances which had long been used in the manufacture of common chemicals. Its characteristic appearance when set free, either in the gaseous or solid state, and the ease with which its liberation is effected, make the fact that it was not observed earlier the more noteworthy.

Iodine was discovered by Bernard Courtois, a nitre manufacturer, of Paris. Bernard Courtois was born at Dijon in 1771. Entering a pharmacy in Auxerre at the age of eighteen, he moved subsequently to Paris, where he worked in the laboratory of Fourcroy at the Ecole Polytechnique, and, after a period of service in the Army, in that of Thenard. He thus became, as is shown by the testimony of his friends, a very able and skilful worker.

During the Napoleonic wars, when France was fighting single-handed against the rest of Europe, great difficulty was experienced in obtaining sufficient imported saltpetre for the manufacture of the immense quantity of gunpowder needed. This led to nitre beds being constructed in various parts of the country, from which the saltpetre was obtained artificially. One of the first of these nitre beds had been set up at Dijon by Courtois' father, and in 1804 Bernard himself established some near Paris, and began the manufacture of nitre on a considerable scale. For the purpose of decomposing the calcium nitrate obtained from the nitre beds he used the alkaline lye of vareck or kelp, the ash obtained by incinerating various sea-plants, which contains both potassium and sodium carbonate (compare Lavoisier, "Sur la Cendre qu'emploient les Salpêtriers de Paris et sur son usage dans la Fabrication du Salpêtre," *Mémoires de l'Académie Royale des Sciences*, 1777, p. 123). When working on a large scale he noticed that the copper vats, in which the nitrate of calcium was decomposed, became very quickly eaten through. He naturally tried to ascertain what caused this corrosion of the metal, and soon found that it was due to the copper combining with a substance, the nature of which was unknown to him. In order to obtain some quantity of this new body he undertook a careful examination of all the materials he used, and this resulted in his discovery of iodine.

Iodine has been manufactured on a commercial scale almost from the time of its first isolation, and it is not pleasant to recall that Courtois did not profit by his discovery. He died in poverty and misery. He had invested the whole of his capital in his works, and when the French ports were thrown open after 1815 potassium nitrate, which could be imported from India more cheaply than it could be made from the nitre beds, was placed on the market in such quantity that his business was entirely ruined ("Etudes Biographiques pour Servir à l'Histoire des Sciences," par Paul Antoine, cap. Paris, 1857). He subsequently attempted to manufacture iodine, but as the demand for it was at that time small and the process for

its extraction not thoroughly worked out it was not a commercial success. He received help from his friends, and in 1831, on the initiative of Thenard, the Academy of Sciences awarded him a prize of 6000 francs for his discovery of iodine. In 1838 he died, leaving to his widow and son, as his biographer remarks, "nothing but a name justly celebrated."

At the time he discovered iodine Courtois was too busily employed as a chemical manufacturer to study it with thoroughness; he did little more therefore than isolate it and ascertain some of its more obvious properties. He, however, sent specimens of it to several of his friends, and Desormes and Clement at his request continued the investigation. It was shortly afterwards handed over for more complete study to Gay-Lussac, perhaps the most distinguished chemist of his day. About two years after Courtois had made his discovery, it was announced at a meeting of the Institut Imperial de France on November 29th, 1813, by Desormes and Clement, and the following summary of the proceedings appeared in *Le Moniteur Universel* for Thursday, December 2nd, 1813:—"Imperial Institute de France—MM. Desormes and Clement showed on Monday last, November 29th, to the physical and mathematical section a very singular substance, discovered in the ash of vareck by M. Courtois, a nitre manufacturer of Paris. Its most remarkable property is that on being subjected to a slight heat it yields a superb violet vapour. It has the aspect of a metal, and yet is easily converted into this violet vapour. Oxygen and carbon have no action upon it at a red heat, but hydrogen reacts with it and produces muriatic acid,* as does also phosphorus. It directly attacks and combines with metals without effervescence; it also unites with oxides, forming compounds, almost all of which are soluble in water. With ammonia it gives a powder which explodes on being touched. The investigation of this new substance is being continued, and its nature will in all probability soon be ascertained."

A fuller account of the discovery is given under the title "Discovery of a New Substance in Vareck," by B. Courtois, in the *Annales de Chimie* (1813, lxxxviii., 304) as follows:—"The mother-liquors of the lye obtained from vareck contain a tolerably large quantity of a singular and curious substance. It can easily be obtained. For this purpose it is sufficient to pour sulphuric acid upon the mother-liquor and to heat the whole in a retort connected with a receiver. The new substance which, on the addition of the sulphuric acid, is at once thrown down as a black powder is converted on heating into a vapour of a superb violet colour; this vapour condenses in the tube of the retort and in the receiver in the form of brilliant crystalline plates, having a glance equal to that of crystallised lead sulphide. On washing these plates with a little distilled water the substance is obtained in a state of purity. The wonderful colour of its vapour suffices to distinguish it from all other substances known up to the present time, and it has further remarkable properties which render its discovery of the greatest interest."

On Monday, December 6th, four days after the announcement of Courtois' discovery had been made, and before the excitement consequent upon it had subsided, Gay-Lussac, who had been some while earlier entrusted by Clement with the further investigation of the substance, read a paper on the subject to the Institut Imperial de France, in which he gave a preliminary account of the experiments he had made and the conclusions which he had reached up to that date.

His views on a matter of such general interest would of course at once become known to most scientific men in Paris, so that we may fix December 6th as the time at which they became public property. The following account of his communication is taken from *Le Moniteur Universel* for Sunday, December 12th, 1813, where t

* This mistake of Desormes and Clement was corrected by Gay-Lussac in the communication which he made to the Institute at its meeting on the following Monday, December 6th.

appears under the heading "Institut Imperial de France (Classe des Sciences Physiques et Mathématiques)":—

"The new substances discovered by M. Courtois, and referred to in one of the preceding sheets, has recently been the subject of an investigation by M. Gay-Lussac, who was invited to undertake it by his friend M. Clement. We shall limit ourselves here to describing the chief results which he has obtained. The new substance, to which the name *iode* might be given, displays in a high degree the electrical properties of oxygen and of oxygenated muriatic acid. After purification by potash and distillation it is infusible at the temperature of boiling water, in which it is nearly insoluble. Treated in every chemical way possible it yields no trace of muriatic acid."

A short summary of Gay-Lussac's results is then given, showing the resemblance of the new substance to chlorine. Attention is drawn to its power of uniting with metals, to its combination with phosphorus, and to the liberation of a new gaseous acid by the action of water on the compound thus produced. A description is given of this new acid, note is made of the fact that it is decomposed by chlorine, the parent substance being again liberated, and of the fact that metals act upon it, liberating hydrogen in bulk equal to half the volume occupied by it in the gaseous state. The formation of the gaseous acid by the union at a high temperature of hydrogen and the new substance is mentioned, as are also the facts that it is formed with liberation of sulphur when the new substance decomposes hydrogen sulphide, and together with sulphuric acid when the new substance reacts with sulphurous acid. It is also recorded that the new substance is not affected by heating with charcoal or by sulphuric acid. The summary concludes:—

"After this account one can only compare *iode* with *chlore*, and the new gaseous acid with muriatic acid. . . . The phenomena of which we have just spoken can all be explained either by supposing that *iode* is an element and that it forms an acid when it combines with hydrogen, or by supposing that the latter acid is a compound of water with an unknown substance, and that *iode* is this substance combined with oxygen. Considering all the facts recounted, the first view appears more probable than the other, and serves at the same time to give probability to that hypothesis according to which oxygenated muriatic acid is regarded as a simple body. Adopting this hypothesis hydriodic acid appears a suitable name for the new acid."

It is seen from this communication that by December 6th Gay-Lussac had placed beyond doubt the elementary nature of iodine and its close relationship to chlorine, and that he had applied to it and to its compound with hydrogen the names by which they are still known.

At this time Humphry Davy, who by special favour of Napoleon had obtained permission to cross France in order to visit Italy, was in Paris, where he had been received by French scientists with the greatest courtesy and consideration. Courtois had distributed a few specimens of the new substance among some of his friends, and a small quantity had come into the possession of Ampère through Clement. Ampère called on Davy on November 23rd, and thinking thus to honour a distinguished foreign guest, gave some to him, possibly at Clement's suggestion. Davy, in the intervals between fêtes, levées, and visits of ceremony, made within a fortnight a hurried examination of this specimen, working mainly at his hotel and for one day in the laboratory of a friend.

Davy's action in thus making use of a courteous attention on the part of Ampère appears to have commended itself to his brother and biographer, Dr. John Davy, for in a note appended to Davy's account of this research, reprinted in his collected works, he says—"This paper on Iodine was the first he communicated after leaving England. The author's love of research, and his zeal in prosecuting it, were strongly shown by his labours whilst on the Continent, especially taking into consideration the very limited means of experimenting which he then commonly had at his disposal, and which were comprised in the contents of two small boxes, one 20 inches long, 7 wide, and 4 high, used

for holding tests, the other 12 inches long, 7½ wide, and 6 high, for holding instruments, as glass tubes, small receivers, retorts and capsules, a blowpipe apparatus, a small pneumatic trough, a delicate balance, and a few other necessary articles."

To do Davy justice, however, he appears to have felt that his intrusion into a field of work upon which he knew that others were engaged required some excuse, for when describing his results in a communication to the Royal Society, he says,—“But as the mode of procuring the substance is now known to the chemical world in general, and as the combinations and agencies of it offer an extensive field for inquiry and will probably occupy the attention of many persons, and as the investigation of it is not pursued by the discoverer himself nor particularly by the gentleman to whom it was first communicated, I shall not hesitate to lay before the Royal Society an account of the investigations I have made upon it, and I do this with the less scruple as my particular manner of viewing the phenomena has led me to some new results which probably will not be considered by the Society as without interest in their relation to the general theory of chemistry and in their possible application to some of the useful arts."

Davy reached the same conclusion as Gay-Lussac, possibly independently, although, as in the case of chlorine, Gay-Lussac's results were at his disposal in writing up his account of his work. He published the details of his observations in a letter addressed to M. le Chevalier Cuvier, dated Paris, December 11th, 1813, which was read at a meeting of the Institute held on December 13th, 1813, and in a fuller and more elaborately written account (*Phil. Trans.*, 1814, 74) which was sent to the Royal Society. The latter was not read at the Society until January 20th, 1814, although it is dated Paris, December 10th.

Davy's work done under such astonishing conditions only confirmed Gay-Lussac's results, and his paper would probably have received little notice had it not been that in it Courtois' discovery was first made known to English readers.

Davy altered Gay-Lussac's name of *iode* into *iodine* to bring it into agreement with chlorine and fluorine.

The attention of chemists everywhere had by this time been drawn to the new element, and communications dealing with it followed rapidly. On December 20th, 1813, Gay-Lussac read to the Institute a further memoir upon its combinations with oxygen (*Annales de Chimie*, lxxviii., 319). On March 21st, MM. Colin and Gauthier de Claubry, who worked under Gay-Lussac's direction in his laboratory, presented their researches on the action of iodine on organic matters; on June 4th Vauquelin published an account of some experiments with the compounds which iodine forms with ammonia, iron, mercury, and alcohol; and, finally, on August 1st, 1814, Gay-Lussac read his famous paper at the Institute (*Annales de Chimie*, 1814, xci., 5—160). In this the whole chemical behaviour of iodine is described in such a masterly fashion that it remains to this day a model of what such an investigation ought to be.

Davy's action in writing to Cuvier and to the Royal Society, and a paragraph referring to it in a Scotch journal, very justifiably roused the indignation of Gay-Lussac, who deals with the matter as follows under the heading "Historical Note on the Discovery of Iodine" in his memoir on iodine mentioned above (*Annales de Chimie*, 1814, xci.):—"About two years after Courtois had made his discovery of iodine, on November 29th, 1813, Clement announced it to the Institute. Courtois had observed several of its properties, particularly its power of forming a very explosive powder when treated with ammonia. He at first proposed to investigate it himself, but being too much occupied with the manufacture of saltpetre to take up laboratory work, he requested Clement to continue his researches. Clement, from similar reasons, could only devote a short time to it, but nevertheless obtained a large number of results, as one sees by the note that was printed

in the *Annales de Chimie*, lxxxviii., 304. He discovered that a gaseous acid is obtained on bringing iodine into contact with damp phosphorus, but he concluded from his experiments that this gas was composed of about one-fourth muriatic acid and one-fourth of iodine (*Moniteur*, December 2, 1813). When Davy came to Paris Clement was still busied with his researches, and thought he could not better receive so distinguished a savant than by showing him the new substance, which he had hitherto shown only to Chaptal and Ampère. I recall these circumstances to reply to the following strange assertion found in the journal of Nicholson and Tilloch, No. 189, p. 69:— 'It appears that iodine was discovered about two years ago, but such is the deplorable state of those who cultivate science in France that nothing had been published until the arrival of our English philosopher in that country.' It is Davy of whom they speak. A little time after having shown iodine to Davy, and having communicated to him the result of his researches, Clement read his note at the Institute, and ended it by announcing that I was continuing the investigation. In fact, on the 6th of December, I read a paper at the Institute which was printed in the *Annales de Chimie*, lxxxviii., 311: I will only recall here that the results it contains determined its nature, and that I there established that this substance is a simple body analogous to chlorine. It has not till now been contested that I first recognised the nature of iodine, and it is certain that Davy only published his results more than eight days after having known mine."

To sum up. Courtois discovered iodine and prepared it in a pure state; Gay-Lussac thoroughly investigated it, demonstrated its close relationship to chlorine, established its elementary nature, and named it. Davy did little more than make these discoveries known in England.

THE POTENTIAL ENERGY OF THE ELEMENTS.

By DANIEL J. RANKIN.

SINCE the values for the potential energy of the elements are functionals of the atomic weights, and a change in the second decimal place of the latter affects, in some instances, two integers in the value of the potentials, it is necessary that the potentials should be subject to revision concomitantly with the atomic weights.

The values previously given were calculated from values of atomic weights taken from Newth's "Inorganic Chemistry," 1905. The potentials in the accompanying table are calculated from the values given for 1909 in the *CHEMICAL NEWS*.

The elements appear to be naturally divided into eleven groups of one or more families. The families are differentiated fundamentally by the density of the ponderable equilibrated or static energy; the density being a constant for all the members of a family. The members of a family are differentiated fundamentally by accretion of mass of static energy and concomitant decrease of potential.

For example, family *a* of Group XI. comprises the elements Gl, Pd, Gd, Pt. The density of the static energy of each of these elements is 43.9, i.e., 1 cc. of the static energy in each weighs 43.9 grms.

The grm.-atom of glucinum has therefore a volume of static energy equivalent to $\frac{9.1}{43.9} = 0.2$ cc., its atomic volume $= \frac{9.1}{2.1} = 4.3$ cc.

Therefore the relative volume of its potential energy $= 4.3 - 0.2 = 4.1$ cc.

Similarly the values of the members of the family are:—

		Atomic vol.	Vol. of potential.	Vol. of static.
		Cc.	Cc.	Cc.
Gl		4.3	4.1	0.2
Pd		9.3	6.9	2.4
Gd		9.2	5.7	3.5
Pt		9.0	4.6	4.4

If we represent these values by concentric circles having the diameters of spheres of similar volumes, the inner circle representing the volume of static and the outer circle the atomic volume, the relative magnitudes of the two states of energy in the ultimate atoms of elements may be compared diagrammatically.

Chemical combination appears to be the result of the mutual attraction of the central ponderable masses of static energy in conformity with the universal law of masses.

Let Fig. 1 represent two contiguous atoms; each central mass of static energy is surrounded by an elastic and

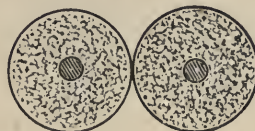


FIG. 1.

penetrable zone of potential energy. The chemical affinity of the two atoms is an expression of the attraction between the two central masses of static energy. Its value is directly as the product of the masses and inversely as the square of the distance separating their centres, ratios for both of which admit of calculation.

The resistance offered to the approach of the static masses by the zones of potential is directly as the density of the latter and the density of the potential is, within certain limits, inversely as the temperature.

Thus, if the two contiguous atoms are in the most dense state as solids, the resistance offered by the density of the potential prevents a passage of the static masses and no combination takes place. If by the accretion of external energy, whether thermal or otherwise, the density of the zones of potential becomes so reduced that the attraction of the masses exceeds the resistance to their conjunction, the masses will be brought into immediate contact, the potential around each coalescing in a manner analogous to two beads of mercury, and the combination will present the form of Fig. 2. In which the two central masses of



FIG. 2.

static energy are surrounded by a single zone of potential; a certain amount of work has, however, to be performed by the mass of static energy in overcoming the resistance due to the density of the zone of potential passed through. This work is evidenced in the heat of formation.

The system resulting from this intrapenetration of masses of static energy and coalition of their atomic potentials constitutes a molecule.

In this view the hypothesis of an interatomic fluid, such as ether, appears unnecessary. In the table of the elements I have designedly omitted mention of the extremely important position of radio-active elements in their relation to the more stable elements,

Also of the many theoretic intermediate elements represented by blanks in Mendeleeff's system, all of which admit of calculation, both for atomic weights and densities.

The Potential Energy of the Elements corrected by the Atomic Weights of 1909.

(Roman figures represent groups; italics, families; K, potentials as large calories per grm.-atom; D.S., density of static energy).

		K.	D.S.
I. a.	H	522564	1.6
II. a.	Li	75501	
	K	13517	
	Rb	6185	4
	Cs	2619	
III. a.	He	134278	
	Na	23353	
	Ca	13397	6.4
	Sr	6130	
	Ba	2508	
IV. a.	Al	14553	6.6
b.	Ne	28033	
	Kr	6854	7.3
	X	3245	
V. a.	F	29087	
	Cl	15585	11.5
	Br	6915	
	I	3212	
VI. a.	Mg	24371	
	Sc	13440	
	Zr	6542	12
	La	3060	
	Yb	1809	
b.	S	17114	
	Se	6930	
	(Te)	3288	15.6
	Tm	1630	
	Te	3058	
c.	Ti	12373	
	Y	6540	
	Ce	3028	16.8
	Lu	1770	
	Th	455	
d.	V	11819	
	Nb	6472	
	Pr	3122	20
	Ta	1638	
VII. a.	N	39622	
	P	17894	
	As	7396	22.2
	Sb	3636	
	Er	1876	
	Bi	1001	
b.	Si	19124	
	Ge	7465	
	Sn	3559	23
	Pb	965	
c.	Al	19445	
	Ga	7539	
	In	3628	23.9
	Dy	1840	
	Tl	965	
VIII. a.	Cr	11813	
	Mo	6412	
	Nd	3065	23.96
	W	1629	
	U	437	
b.	Mn	11319	
	Sa (see Note) .	(2860)	24

		K.	D.S.
IX. a.	O	38912	24.9
b.	Fe	11188	25.3
c.	Ni	10689	26.5
d.	Co	10655	26.8
X. a.	Zn	7682	
	Cd	3500	
	Tb	1788	29.7
	Hg	950	
b.	Cu	7730	
	Ag	3622	39.4
	Au	953	
XI. a.	Gf	52940	
	Pd	3581	
	Gd	1712	43.9
	Pt	949	
b.	B	43199	
	Rh	3718	47.5
	Ir	949	
c.	C	39050	
	Ru	3710	
	Eu	1757	48.8
	Os	953	

NOTE.—The atomic weight given for Sa, 150.4, is too high; a probably more approximate weight is 146, giving a potential 3056 K. An atomic weight of 150.4 would indicate a compound element analogous to Te. Sa is the analogue of Nd in the chromium family.

OSMOTIC PHENOMENA AND THEIR MODERN PHYSICAL INTERPRETATION.*

By Prof. H. L. CALLENDAR, M.A., LL.D., F.R.S.

OSMOTIC pressure is a phenomenon of such importance in the theory of solutions, and in the interpretation of all vital processes, and so much valuable work has recently been directed to its elucidation, that, although it is a somewhat thorny and difficult subject, no apology is needed for any serious attempt, however inadequate, at its explanation.

One of the earliest recorded experiments on osmotic pressure is that of the Abbé Nollet, who found that a bladder containing alcohol, when immersed in water, absorbed water so greedily as in many cases to burst the bladder. The experiment illustrates in an imperfect manner the fundamental property of all animal and vegetable membranes of allowing some substances to pass through them by osmosis more easily than others. In many cases such membranes, while freely permeable to water, are practically impermeable to certain substances in solution, and play the part of sieves in directing and controlling diffusion. It will readily be understood that results of the greatest importance to biology have been obtained by studying this property of *semipermeability*, as it is called, but the application of natural membranes to the physical study of the subject is necessarily limited on account of the difficulty of obtaining sufficiently large and perfect membranes capable of withstanding any considerable pressure.

Artificial membranes of sufficient fineness to be impermeable to such substances as sugar in solution, were first prepared by Traube by means of precipitated pellicles of substances like copper-ferrocyanide. The first quantitative measurements of osmotic pressures of considerable magnitude were made by Pfeffer with membranes of this kind deposited in the pores of earthenware pots fitted with suitable manometers for indicating the pressure developed. Pfeffer found that when a semipermeable vessel, filled with

* A Discourse delivered at the Royal Institution, February 26, 1909.

sugar solution, was immersed in water, the membrane being freely permeable to water, but not to the dissolved sugar, the solution absorbed water through the membrane by osmosis until the internal pressure reached a certain magnitude sufficient to balance the tendency to absorption. The osmotic pressure developed in the state of equilibrium was found to be proportional to the strength of the solution, and to increase with rise of temperature at the same rate as the pressure of a gas at constant volume. A few years later van't Hoff, reviewing these experiments in the light of thermodynamics, showed that the osmotic pressure of a dilute solution should be the same as the pressure exerted by a number of molecules of gas equal to those of the dissolved substance in a space equal to the volume of the solution, that it should be the same for all solutions of equal molecular strength, and that osmotic pressure followed the well-known laws of gas-pressure in all respects. The most important generalisation was hailed as the first step to a complete kinetic theory of solution, and the osmotic pressure itself has generally been regarded as due to the bombardment of the sides of the semi-permeable membrane by the particles of solute, as though they were able to move freely through the solution with velocities comparable to those of the molecules of a gas. Such a view would not now be seriously maintained, but the fascinating simplicity of the gas-pressure analogy has frequently led to the attempt to express everything in terms of the osmotic pressure, regarded simply, but inaccurately, as obeying the gaseous laws, and has done much to divert attention from other aspects of the phenomena, which, in reality, are more important and have the advantage of being more easily studied. It was very soon discovered that the gaseous laws for osmotic pressure must be restricted to very dilute solutions, and that the form of the laws was merely a consequence of the state of extreme dilution, and did not necessarily involve any physical identity between osmotic pressure and gas-pressure. Many different lines of argument might be cited to illustrate this point, but it will be sufficient to take some of the more recent experimental measurements of osmotic pressure by the direct method of the semi-permeable membrane.

Morse and Frazer in 1905 succeeded in preparing ferrocyanide membranes impermeable to sugar, and capable of withstanding pressures of more than 20 atmospheres. They operated by Pfeffer's original method, allowing water to diffuse into the solution in a porous pot until the maximum pressure was developed. There are many serious experimental and manipulative difficulties which the authors carefully considered and discussed in applying this method, but they succeeded in obtaining very consistent results. As a first deduction from their investigations they considered that they had established the relation that the osmotic pressure of cane-sugar was the same as that exerted by the same number of molecules of gas at the same temperature in the volume occupied by the solvent, and not in the volume occupied by the solution. In other words, the osmotic pressure of a strong solution was greater than that given by van't Hoff's formula for a dilute solution in proportion as the volume of the whole solution exceeded the volume of the solvent contained in it. It was a very natural extension of the gas-pressure analogy to deduct the volume occupied by the sugar molecules themselves in order to arrive at the space in which they were free to move. Unfortunately, the later and more accurate series of measurements by the same experimentalists at 0° C. and 5° C., gave nearly the same osmotic pressures as at 24° C., and would appear to show, either that there is little or no increase of osmotic pressure with temperature, and that the pressures at 0° C. are much greater than those given by their extension of the gas-pressure analogy, or that one or other of the series of experiments are in error.

About the same time Lord Berkeley and E. J. Hartley undertook a series of measurements of the osmotic pressures of solutions of various kinds of sugar at 0° C. by a greatly improved experimental method, which permitted

the range of pressure to be extended to upwards of 100 atmospheres. Instead of allowing the solvent to diffuse into the solution until the equilibrium pressure was reached, they applied pressure to the solution until balance was attained. The method of Lord Berkeley and Hartley possesses several obvious advantages, and it is impossible to study the original memoir without being convinced that they have really measured the actual equilibrium pressures with an order of certainty not previously attained or even approached. The pressures found were in all cases greatly in excess of those calculated from the gas-pressure of the sugar molecules in the volume occupied by the solution (according to van't Hoff's formula for dilute solutions), or even in the restricted volume occupied by the solvent (according to Morse and Frazer's assumption).

Lord Berkeley endeavoured to represent these deviations on the gas-pressure analogy by employing a formula of the van der Waals type, with three disposable constants. Out of some fifty formulæ tested, the two most successful were those given in Table I. The constants A, a, and b were calculated to fit the three highest observations for each solution. Values calculated by the formulæ for the lower points were then compared with the observations at these points, with the results given in Table I. for cane-sugar. It is at once evident that, even with three constants, the gas-pressure analogy does not represent the results satisfactorily within the limits of error of experiment. Moreover, with three constants the equation cannot be interpreted, so that the gas-pressure analogy becomes useless as a working hypothesis, or as a guide to further research. On the vapour-pressure theory, to be next explained, the results are much better represented, as shown in line C, with but a single constant, and that a positive integer with a simple physical meaning.

Vapour-pressure Theory.

On the vapour-pressure theory, osmotic equilibrium depends on equality of vapour-pressure and not on an imaginary pressure which the particles of the dissolved substance would exert if they were in the state of gas at the same volume and temperature. The vapour-pressure of any substance is a definite physical property of the substance which is always the same under the same conditions of pressure and temperature and state, and is easily measured in most cases for liquids and solutions. Equality of vapour-pressure is one of the most general, as well as the simplest, of all conditions of physical equilibrium. Ice and water can only exist together without change under atmospheric pressure at the freezing-point 0° C., at which their vapour-pressures are the same. Below the freezing-point the vapour-pressure of water is greater than that of ice. Either is capable of stable existence separately within certain limits, but if the two are put in communication, the vapour, being mobile, passes over from the water at higher pressure to the ice at lower pressure until equality of vapour-pressure is restored by change of temperature, or until the whole of the water is converted into ice.

TABLE I.—Osmotic Pressures of Cane-sugar Solutions.
(Osmotic pressures calculated by various formulæ).

Van't Hoff	..	..	35.6	27.6	19.7	11.2
Morse and Frazer	..	..	53.2	37.4	24.4	13.3
Lord B. (1)	..	..	68.4	45.0	27.7	14.6
Lord B. (2)	..	..	67.7	43.4	25.4	12.2
C.	..	..	67.6	43.7	26.8	14.1
Do. observed, Lord B.	..	..	67.5	44.0	26.8	14.0

Lord Berkeley's equations:—

$$(A/v - P + a/v^2)(v - b) = RT \quad \dots (1).$$

$$(A/v + P - a/v^2)(v - b) = RT \quad \dots (2).$$

In the case of ice and water, equality of vapour-pressure can also be restored by a suitable increase of pressure. This is the well-known phenomenon of the lowering of the freezing-point by pressure. By considering the equilibrium of water and vapour in a capillary tube, Lord Kelvin

showed that the vapour-pressure of water, or any other liquid, was increased by pressure according to a very simple law, the ratio of the increase of vapour-pressure, dp , to the increase of pressure, dP , on the liquid being simply equal to the ratio of the densities of the vapour and liquid, or inversely as the specific volumes, v and V . This relation, which may be written $VdP = vdp$, is merely a special case of Carnot's principle, and was deduced by assuming the impossibility of perpetual motion. Assuming a similar relation to apply to ice, Poynting showed that when a mixture of ice and water was subjected to pressure, the vapour-pressure of the ice must be increased more than that of the water (since the specific volume of ice is greater than that of water). Consequently, some of the ice must pass over into water, and the temperature must fall until the vapour-pressures are again equal. The lowering of the freezing-point by pressure, as observed by Lord Kelvin, and calculated by James Thomson, agrees precisely with that deduced as above from the condition of equality of vapour-pressure.

Similar considerations apply to the equilibrium between a solution and the pure solvent, or between solutions of different strengths. To take a simple case, the vapour-pressure p'' of a sugar solution is always less than the vapour-pressure p' of water at the same temperature, and the ratio p''/p' of the vapour-pressures depends simply on the concentration of the solution, diminishing regularly with increase of concentration, and being independent of the temperature. If separate vessels containing solution and water are placed in communication at the same temperature by a tube through which the vapour has free passage, vapour will immediately pass over from the water to the solution in consequence of the pressure difference, and will condense in the solution. The immediate effect is to produce equality of vapour-pressure by change of temperature. This takes only a few seconds. The vapour-pressure then remains practically uniform throughout. As diffusion proceeds and the temperature is slowly equalised, the water will gradually distil over into the solution, but the process of diffusion is so infinitely slow compared with the equalising of vapour-pressure, that the final attainment of equilibrium would take years unless the solution were continually stirred.

The reason why equality of vapour-pressure is so important as a condition of physical equilibrium is that the vapour is so mobile and so energetic as a carrier of energy in the form of latent heat. The first effect is generally a change of temperature, but if the temperature is kept constant, there must then be a change of concentration. Thus, if two parts of the same solution are maintained at different constant temperatures, the concentrations will change so as to restore equality of vapour-pressure, if possible. Thus in a tube of solution, the two ends of which are maintained at different temperatures, the dissolved substance will appear to move towards the hotter end. What really happens is that the vapour, which is the mobile constituent, moves towards the colder end. If the tube is horizontal, with a free space above the liquid for the vapour, this transference will be effected with extreme rapidity. In fact, it will be practically impossible to establish an appreciable difference of temperature until the transfer is effected. If the vapour has to diffuse through the solution in a vertical column heated at the top, the process is greatly retarded, but the final effect is the same, and can be readily calculated from the relation between the vapour-pressure and the concentration.

In explaining the production of osmotic pressure as a necessary consequence of the laws of vapour-pressure, there is one difficulty which, though seldom expressed, has undoubtedly served very greatly to retard progress. How can an insignificant difference of vapour-pressure, which may not amount to so much as one-thousandth part of an atmosphere in the case of a strong sugar solution at 0°C ., be regarded as the cause of an osmotic pressure exceeding 100 atmospheres, or 100,000 times as great as itself? The answer is that the equilibrium does not depend at all on

the absolute magnitude of the vapour-pressure, but only on the work done for a given ratio of expansion, which is the same in the limit for a grm.-molecule of any vapour at the same temperature, however small the vapour-pressure. Indirectly, the smallness of the vapour-pressure may have a great effect in retarding the attainment of equilibrium, especially if obstructive influences, such as other vapours or liquids, are present. Thus, mercury at ordinary temperatures in the open air is regarded as practically non-volatile. Its vapour-pressure is less than a millionth of an atmosphere, and cannot be directly measured, though it may easily be calculated. When, however, we take mercury in a perfect vacuum, such as that of a Dewar vessel, the presence of the vapour is readily manifested by its rapid condensation on the application of liquid air in the form of a fine metallic mirror of frozen mercury. The least trace of air or other gas in the vacuum will retard the condensation excessively.

Under the conditions of an osmotic-pressure experiment we have solvent and solution in practical contact, separated only by a thin porous membrane. It will facilitate our conception of the conditions of equilibrium if we imagine the membrane to be a continuous partition pierced by a large number of very fine holes of the order of a millionth of an inch in diameter. If the holes are not wetted by the solution or the water, the liquid cannot get through unless the pressure on it exceeds 100 atmospheres, but the vapour has free passage. If the solvent and solution are under the same hydrostatic pressure, the vapour-pressure of the solvent will be the greater, and the vapour will pass over into the solution. Since the surfaces are practically in contact, no appreciable difference of temperature can be maintained. If the solution is confined in a rigid envelope, so that its volume cannot increase, the capillary surfaces of the solution will rapidly bulge out as the vapour condenses on them, and the pressure on the solution will increase until condensation finally ceases, when the vapour-pressure of the solution is raised to equality with that of the pure solvent. The osmotic pressure is simply the mechanical pressure-difference which must be applied to the solution in order to increase its vapour-pressure to equality with that of the pure solvent. If any pressure in excess of this value is applied to the solution, the vapour will pass in the opposite direction, and solvent will be forced out of solution. The osmotic work required to force a grm.-molecule of the solvent out of the solution is the product of the osmotic pressure P by the change of volume U of the solution per grm.-molecule of solvent abstracted. In the state of equilibrium of vapour-pressure, this osmotic work PU must be equal to the work which the vapour could do by expanding from the vapour-pressure p' of the pure solvent to the vapour-pressure p'' of the solution. Neglecting minor corrections, we thus obtain the approximate relation—

$$PU = R\theta \log (p'/p'').$$

(Obtained by integrating $UdP = vdp$; Planck, "Thermodynamik," also *Zeit. Phys. Chem.*, 1902, xii., 212, and 1903, xlii., 584).

From this point of view the osmotic pressure of a solution is not a specific property of the solution in the same sense as the vapour-pressure, or the density, or the concentration, but is merely the mechanical pressure required under certain special conditions to produce equilibrium of vapour-pressure when neither the temperature nor the concentration are allowed to vary. One might with almost equal propriety speak of the "osmotic temperature" of a solution, meaning by that phrase the difference of temperature required to make the vapour-pressure of the solution equal to that of the pure solvent. The observation of the elevation of the boiling-point of a solution above that of the pure solvent is a familiar instance of a special case of such a temperature difference. It is just as much a specific property of the solution as the osmotic pressure, and would only require a perfectly non-conducting membrane for its production. No one would regard the

rise of boiling-point as being the fundamental property of a solution in terms of which its other properties should be expressed. By similar reasoning osmotic pressure should not be regarded as existing *per se* in the solution, and as being the cause of the relative lowering of vapour-pressure and other phenomena. This point of view does not detract in any way from the reality and physical importance of the effects of osmotic pressure when it comes into play, but it puts the phenomena in their true light as consequences of the law of vapour-pressure.

Regarded as a verification of the laws of vapour-pressure, direct measurements of the osmotic pressure are of the highest value, but there are comparatively few cases known at present in which such direct measurements are possible. In other cases the osmotic pressure, if it exists, can always be calculated from a knowledge of the vapour-pressure. For the elucidation of osmotic phenomena and many other problems in the theory of solutions, we are compelled to make a systematic study of the relations of vapour-pressure. Much has been done in this direction in the past, but owing to the difficulty of the measurements, much remains yet to do. I may therefore be pardoned if I allude briefly to some of the methods which I have employed for this purpose, and some of the conclusions at which I have so far arrived.

It is often a difficult matter, when the difference of vapour-pressure between a solution and the solvent is small, to measure the pressure difference directly to a sufficient degree of accuracy. A method very commonly employed, which has been brought to a high degree of accuracy by Lord Berkeley and his assistants, depends on the observation of the losses of weight of two vessels, containing solution and solvent respectively, when the same volume of air is aspirated slowly through them in succession. To secure accurate results, the air must pass very slowly. One complete observation takes about a week to perform successfully, and involves many difficult manipulations. I have endeavoured to avoid this difficulty by measuring the temperature difference in place of the pressure difference, since the temperature difference remains nearly constant, while the pressure difference tends to diminish in geometrical progression with fall of temperature. The method adopted for this purpose is that indicated in the diagram of the Vapour-temperature Balance. The temperatures of solution and solvent, contained in separate vessels communicating through a tap, are adjusted, until, on opening communication between them, there is no flow of vapour from one to the other, as indicated by a change in the reading of a pair of thermo-junctions immersed in the solvent respectively. The corresponding difference of temperature is observed, and since the vapour-pressures of the solvent are known, it is easy to calculate the required ratio or difference of the vapour-pressures of solvent and solution at the same temperature. When the vapour-pressures are very small, it may be difficult to observe the change of temperature on opening the tap, unless the apparatus is very carefully exhausted. A more delicate method in this case is to observe the direction and magnitude of the current of vapour from solution to solvent, or *vice versa*, by means of the "Vapour-current Indicator," illustrated in the companion diagram. This consists of a delicately suspended vane, the deflections of which are read by a mirror, and will readily indicate a difference of pressure less than the thousandth part of a millionth of an atmosphere.

The vapour-current indicator is so constructed that its deflections are very accurately proportional to the pressure difference, much more so in fact than any form of electric galvanometer. It can also be employed for direct measurements of small differences of vapour-pressure. The chief difficulty in this case is to ensure the absence of air or other disturbing factors. A method of avoiding this difficulty is to work at atmospheric pressure, and to measure the pressure difference between two vertical columns of air saturated with the vapours of the solvent and solution respectively. (I first showed this experiment ten years

ago, in illustration of the delicacy of the apparatus, at a Friday Evening Lecture at the Royal Institution). The temperature difference may be adjusted to balance, and is preferably measured by means of a pair of differential platinum thermometers, which permits a higher order of accuracy to be attained than the thermo-electric method.

Vapour-pressure in Relation to Molecular Constitution.

The well-known law of Raoult, according to which the relative lowering of vapour-pressure of a solution is equal to the ratio of the number of molecules n of the solute to the number of molecules of solvent N in the solution, has thrown a great deal of light on the molecular state of the dissolved substance in dilute solutions, but fails notably in many cases when applied to strong solutions. In the case of homogeneous mixtures of two indifferent volatile substances, such as benzol (C_6H_6) and ethylene chloride ($C_2H_4Cl_2$), which mix in all proportions without mutual action, a slightly different but equally simple law is known to hold very accurately throughout the whole range of concentration from 0 to 100 per cent. The vapour-pressure of each ingredient is simply proportional to its molecular concentration. In other words, the ratio of the partial vapour-pressure p' of either constituent at any concentration to its vapour-pressure p'_0 in the pure state at the same temperature is equal to the ratio of the number of its molecules n' in the solution to the whole number of molecules $n' + n''$ of both substances in the solution. Such is evidently the form of the simple mixture law. For substances which form compounds in the solution, or whose molecules are associated or dissociated, this simple law is widely departed from. In a recent paper, "On Vapour-pressure and Osmotic Pressure of Strong Solutions" (*Proc. R.S.A.*, 1908, lxxx., 466), I have endeavoured to extend this simple relation to more complicated cases by making the obvious assumption that, if compound molecules are formed, they should be counted as single molecules of a separate substance in considering their effect on the vapour-pressure. With this proviso the vapour-pressures of strong solutions are well represented by a natural extension of the simple mixture law, and it becomes possible to investigate the nature of the compounds formed in any case. To take a simple instance, suppose that each of the n molecules of the dissolved substance combines with a molecules of the solvent, the total number of molecules of the solvent being N . The ratio of the vapour-pressure p' of the solvent in the solution to the vapour-pressure p'_0 of the pure solvent at the same temperature, will then be the same as the ratio of the number $N - an$ of molecules of *free* solvent in the solution, to the whole number of molecules $N - an + n$ in the solution, each compound molecule being counted as a single molecule.

With the simple formula—

$$p'/p'_0 = (N - an + n)/(N - an)$$

the values of the vapour-pressure are very easily calculated from the molecular concentration n for simple integral values of the hydration factor a . The osmotic pressures are also readily deduced from the ratio of the vapour-pressures (p'/p'_0) by the formula—

$$PU = RT \log (p'/p'_0).$$

The value $a=5$ fits the osmotic pressures for cane-sugar very well, as shown in line C. in Table I. The value $a=2$ fits Lord Berkeley's observations on dextrose equally well up to pressures of 130 atmospheres. The same value $a=5$ for cane-sugar also fits the observations on the depression of the freezing-point and the rise of the boiling-point, as it necessarily must, since these phenomena also depend on the vapour-pressure. The freezing-point method is the easiest for getting the ratio of the vapour-pressures to compare with the formula. At the freezing-point of an aqueous solution, the vapour-pressure of the solution must be the same as that of ice, provided that ice separates on freezing in the pure state. The ratio of the vapour-pressure of ice to that of water at any temperature below

0° C. is easily calculated. All the best recorded results, except those of a few associating substances, give simple positive integral values of a . Even in the case of associating substances, like formic acid and acetone, the curves are of the same type, but the value of a is negative. Dissociating substances, like strong electrolytes, present greater difficulties, on account of the ionisation factor. But allowing for the uncertainty of the ionisation data, they seem to follow satisfactorily the same law of vapour-pressure.

It appears from the form of the proposed law that the hydration factor a makes very little difference to the vapour-pressure in weak solutions, which follow Raoult's law as a limiting case, but it makes a very great difference in strong solutions, when nearly all the free water is used up, and the denominator $N - an$ is small. Thus the depression of the freezing-point of a strong solution of calcium chloride is more than five times as great as that calculated from the number of ions present in the solution. Each ion appears to appropriate no less than 9 molecules of water. The factor $a = 9$ gives a very good approximation to the freezing-point curve, as far as the uncertainty of the data permit. When $N = an$, the vapour-pressure would be reduced to zero, according to the formula, but the formula ceases to apply when the vapour-pressure of the compound molecules themselves becomes equal to that of the solution. At or before this point the molecules will dissociate with the formation of lower hydrates. Many analogous phenomena are already known, and a more complete study of the vapour-pressures of strong solutions may be expected to throw additional light on the subject.

The essential point of the theory here sketched is that the equilibrium existing in a solution is one between definite chemical compounds and the solvent, giving rise to a simple vapour-pressure relation by means of which the phenomena may be studied and elucidated. There is a great deal of work to be done before such a theory can be regarded as established, but in the meantime it may serve very well as a working hypothesis for correlating experimental results, and suggesting new lines of investigation. Regarded in this light, the vapour-pressure theory may serve a useful purpose, and judging by the experimental data at present available, I think I may fairly claim to have made out a good *prima facie* case for the theory.

NOTE.—The vapour current indicator is a development of the old smoke-jack. A light spiral vane with a mirror attached is suspended in a tube which nearly fits it by means of a quartz fibre. Joule (*Proc. Phil. Soc.*, Manchester, vii., 35) employed a wire spiral suspended by a silk fibre for indicating air currents, but does not seem to have adapted it for purposes of exact measurement. The instrument shown in the lecture gave a deflection of 30° (500 mm. at 1 metre) for a velocity of air current 0.01 cm./sec. The sensitiveness might easily have been increased, but the above amply suffices for most purposes.

THE SYNTHESIS, CONSTITUTION, AND USES OF BAKELITE.*

By L. H. BAKERLAND, Sc.D.

SINCE many years it is known that formaldehyde may react upon phenolic bodies. That this reaction is not so very simple is shown by the fact, that according to conditions of operating or to modified quantities of reacting materials, very different results may be obtained; so that bodies very unlike in chemical and physical properties may be produced by starting from the same raw materials. Some of these so-called condensation products are soluble in water, other ones are crystalline, while some others are amorphous and resin-like. Then again, among the latter resinous products some are easily fusible and soluble in

alcohol or similar solvents, while other ones are totally insoluble in all solvents and infusible. This paper will deal with a product of the latter class.

The complexity of my subject compels me to make a brief historical outline which will allow us to form a clearer idea of the scope of my work and differentiate it from prior or contemporary attempts in subjects somewhat similar.

That phenols and aldehydes react upon each other was shown as far back as 1872 by Ad. Bayer and others (*Ber.*, v., 1095; xix., 3004 and 3009; xxv., 3477; xxvii., 2411).

The substances obtained by these investigators were merely of theoretical interest and no attempt was made to utilise them commercially; furthermore, their method of preparation was too expensive and too uncertain, and the properties of some of their resinous products were too undecided to suggest the possibility of utilising them for technical purposes.

Until 1891 attempts at synthesis with formaldehyde were generally limited to the use of its chemical representatives, either methylal, methylene acetate, or methylenetaloid compounds.

With the advent of cheap commercial formaldehyde, Kleeberg (*Annalen*, 1891, cclxiii., 283) took up again this subject, using formaldehyde solution in conjunction with phenol and in presence of strong HCl. Under spontaneous heating he obtained a sticky paste, which soon becomes a hard irregular mass. The latter is infusible and insoluble in all solvents and resists most chemical agents; boiling with alkalis, acids, or solvents will merely extract small amounts of apparent impurities.

As Kleeberg could not crystallise this mass, nor purify it to constant composition, nor in fact do anything with it, after it was once produced, he described his product in a few lines, dismissed the subject, and made himself happy with the study of nicely crystalline substances as are obtained by the action of formaldehyde and polyphenols, gallic acid, &c.

The mass obtained after Kleeberg's method is a hard and irregular porous substance containing free acid, which can only be removed with difficulty after grinding and boiling with water or alkaline solutions. The porosity of the mass is due, as we shall see later, to the evolution of gaseous products during the process of heating.

In 1899 Smith (Engl. Pat., Arthur Smith, 16247, August 9, 1899), realising probably that Kleeberg's method does not lend itself to moulding homogeneous articles, tried to moderate the violent reaction by using a solvent like methyl-alcohol or amyl-alcohol, in which he dissolves the reacting bodies, as well as the condensing agent, muriatic acid. Even then the reaction is too violent if formaldehyde be used, so he does not use formaldehyde, but instead he takes expensive acetaldehyde and paraldehyde, or expensive polymers of formaldehyde. After the reaction, he slowly evaporates the mixtures and drives off the solvent at 100° C. He thus obtains, by-and-bye, a hardened mass in sheets or slabs which can be sawed, cut, or polished. In his German patent specification (D.R.P., A. Smith, 112685, October 10, 1899) he insists on the fact that in his process the methyl- or amyl-alcohol not only act as solvents but participate in the reaction, and he states that this is clearly shown by the colour of the final product, which is dependent on the nature of the solvent he employs. He mentions that his drying requires from twelve to thirty hours; my own experience is that it takes several days to expel enough of the solvent; and even after several months there is still a very decided smell of slowly liberated solvent. During the act of drying I observed in every instance warping and irregular shrinking of the mass, which thereby becomes deformed and makes this method unfit for accurate moulding.

In 1902 Luft (D.R.P., Adolf Luft, 140552, April 29, 1902; U.S.P., 735278) tried to overcome these difficulties in a somewhat similar way. Like Kleeberg he uses a mixture of formaldehyde, phenol, and an acid; but recognising the imperfections of the product and desiring to make of it a plastic that can be moulded, he mixes the mass

* Read before the New York Section of the American Chemical Society on February 5, 1909. From the *Journal of Industrial and Engineering Chemistry*, i., No. 3.

before hardening with suitable solvents such as glycerin, alcohol, or camphor. He virtually does the same thing as Smith, with the difference, however, that he adds his solvents *after* the main reaction is partially over and uses his acid condensing agent in aqueous solution. His aim, as clearly expressed in his patent specifications, is to obtain a mass which remains "transparent and more or less plastic." After pouring his mixture in a suitable mould he dries at a temperature of about 50° C. He too insists on the advantages of using solvents, and in his German patent (page 1, line 44) he states that from 2 to 10 per cent glycerin must remain in the mass; moreover, he arranges matters so as to retain in his mixture all the expensive camphor. The whole process of Luft looks clearly like an attempt to make a plastic similar to celluloid, and to prepare it and to use it as the latter. The similarity becomes greater by the use of camphor and the same solvents as in the celluloid process.

I have prepared Luft's product; it is relatively brittle, very much less tough and flexible than celluloid; it does not melt if heated although it softens decidedly; acetone swells it, and suitable solvents can extract free camphor and glycerin from it.

And now we come to an attempt of another kind, namely, the formation of soluble synthetic resins, better known as shellac substitutes.

Blumer (Engl. Pat., Louis Blumer, June 5, 1902, No. 12880) boils a mixture of formaldehyde, phenols, and an oxyacid, preferably tartaric acid, and obtains a fusible, alcohol-soluble, resinous material, which he proposes as a shellac substitute. This substance is soluble in caustic soda lye; it can be melted repeatedly, and behaves like any soluble fusible natural resin. Blumer in his original English patent application puts great stress on the use of an oxyacid, and seems to think that the latter participates prominently in the reaction; he uses it in the proportion of one molecule of acid for two molecules of phenol and two molecules of formaldehyde.

Nathaniel Thurlow, working in my laboratory on the same subject, has conclusively shown several years ago that the identical material can be obtained by the use of minute amounts of inorganic acids; he has shown furthermore that equimolecular proportions are not necessary; in fact they are wrong and harmful if the reaction be carried on in such a way that no formaldehyde be lost; he showed also that in order to obtain a fusible soluble resin, an excess of phenol over equimolecular proportions must be used, unless some formaldehyde be lost in the reaction.

So as to avoid confusion, I ought to mention here that Blumer and Thurlow's resin is relatively very brittle, more so than shellac, and that no amount of heating alone changes it into an insoluble, infusible product.

As to the real chemical constitution of this interesting product which I have tried to establish by indirect synthesis, I shall read a paper on this subject at one of the next meetings of this Society.

About a year later, Fayolle (French Pat., E. H. Fayolle, 335584, September 26, 1903) tries to make gutta-percha substitutes by modifying Luft's method; he adds large amounts of glycerin to the sulphuric acid used as condensing agent, and obtains a mass that remains plastic and can be softened and kneaded whenever heat is applied. On trial, this method gave me a brittle unsatisfactory substance of which it is difficult, if not impossible, to wash away the free acid without removing at the same time much of the glycerin. In this relation, Luft's way of adding the glycerin after eliminating the acid seems more logical. (See also addition patents to original French Pat. add. Pat. 2414, February 8, 1904, and 2485, February 18, 1944; Fayolle).

Later (French Pat., E. H. Fayolle, 341013, March 7, 1904), the same inventor modified his method by adding a considerable amount of pitch ("brai") and oil, thus trying to make another gutta-percha substitute which also softens when heated and remains plastic.

In 1905 Story (Engl. Pat., Henry Story, 8875, 1905) modifies all above methods in the following way:—He discontinues the use of condensing agents and of added solvents; but he takes a decided excess of phenol, namely, three parts of 40 per cent formaldehyde and five parts of 95 per cent cresol or carbolic acid; by this fact the latter is present in excess of equimolecular proportions. He boils this mixture for eight to ten hours, then concentrates in an open vessel which drives off water and some formaldehyde, and which increases still more the excess of phenol; after the mixture has become viscous he pours it into suitable moulds, cools down, and afterwards hardens by slow drying below 100° C., or as stated in his patent, at about 80° C. His product is infusible and insoluble. But this method has some very serious drawbacks which I shall describe summarily, and which Story himself recognised later (see his addition Patent, Belgium, 210965, September 30, 1908).

His process is necessarily slow. Leaving out of consideration his long preliminary boiling, the hardening process at temperatures below 100° C. is really a drying process, where the excess of phenol that provisionally has acted as a solvent is slowly expelled. This assertion I have been able to verify beyond doubt by my direct experiments where hardening was conducted in closed vessels at below 100° C. and where I succeeded in collecting phenol with the eliminated water. The evaporation or drying process may proceed acceptably fast for thin layers, or thin plates, but for masses of a somewhat larger volume it requires weeks and months; even then the maximum possible hardness or strength is not reached at such low temperatures. All this not merely involves much loss of time, but the long use of expensive moulds, a very considerable item in manufacturing methods; furthermore, during the act of drying, the evaporation occurs quickest from the exposed surface, thus causing irregular contraction and intense stresses, the final result being misshapen moulded objects, rents, or cracks.

Story states that if pure phenol be used the reaction proceeds very slowly; I should add that in that case the reaction does not take place, except very imperfectly, even after several days of continuous boiling. Even then in some of my own experiments made with pure commercial crystallised phenol and with commercial 40 per cent formaldehyde, I obtained products not of the insoluble type, but similar to the soluble fusible products of Blumer and Thurlow.

Taken in a broad sense, Story's process is very similar to Luft's, with this difference, however, that he foregoes the use of an acid condensing agent, and instead of using a solvent like alcohol, glycerin, or camphor, he uses a better and cheaper one, namely, an excess of phenol. In further similarity with Luft and Smith's his method is, as he expresses himself in his patent text, a drying process.

Like Smith and Luft he is very careful to specify temperatures not exceeding 100° C. for drying off his solvent.

Shortly after Story filed his patent, DeLaire (French Pat., DeLaire, 361539, June 8, 1905) obtained a French patent for making soluble and fusible resins either by condensing phenols and formaldehyde in presence of acids, in about the same way as Blumer or Thurlow, and then melting this product; or by dissolving phenol in caustic alkalis used in molecular proportions, then precipitating the aqueous solution with an acid, and afterwards resinifying the re-precipitated product by heating it until it melts. I should remind you that the French patent laws allow patents without any examination whatever as to novelty. And I should state also that DeLaire simply uses here the old and well-known processes of Lederer (*Journal Praktische Chemie*, [2], 1, 224) and Manasse (*Ber.*, 1894, 2409; D.R.P., Bayer, 85588; U.S.P., Manasse, 526786, 1894), which consists in making a phenol-alcohol by the action of formaldehyde on an aqueous solution of a phenolate and subsequent treatment with an acid.

It is a well-known fact that these phenol-alcohols, for instance saligenin, if heated alone or with an acid, will

give partial anhydrides such as saliretin and homosaliretin (Beilstein, *Organ. Chemie*, 1896, ii., 1109), $C_{14}H_{14}O_3$ or $C_6H_4(OH)CH_2OC_6H_4CH_2OH$ (R. Piria, *Ann. Chem.*, xlviii., 75; lvi., 37; lxxi., 245; xcvi., 357; Moitessier, *Fahresb.*, 1886, 676), fusible and soluble in alcohol or caustic soda, and precipitable from the latter by the addition of chloride of sodium.

Trisaligenosaligenin, $C_{28}H_{26}O_5$ or $4C_7H_8O_2-3H_2O$ (K. Kraut, *Ann. Chem.*, clvi., 123; Gerhardt, *Ann. Chim. Phys.*, [3], vii., 215), and heptasaligenosaligenin, $C_{56}H_{50}O_9$ or $8C_7H_8O_2-7H_2O$ (F. Beilstein and F. Seelheim, *Ann. Chem.*, cxvii., 83), are both higher anhydrides of similar resinous character, the first one obtained by the action of sulphuric acid on saligenin, the latter by the action of acetic anhydride.

The direct homologue of saliretin, which is methyl-saliretin or homosaliretin, has properties similar to saliretin, melts at 200° or 205° C., and is less soluble (C. Schotten, *Ber.*, 1878, p. 784).

No wonder then if the English (Engl. Pat., DeLaire, 15517, 1905) and the German patents (D.R.P. DeLaire, 19262, July 19, 1905) of DeLaire vary considerably in text and claims from the French patent; the claims are reduced merely to a method consisting in resinifying phenol-alcohols by heating them under reduced pressure or vacuum. The resins of DeLaire are fusible, soluble products, having all the general properties of saliretin and homosaliretin.

In order to complete my enumeration of methods where alkalis are used, I ought to mention two processes which aim at products very different from those which we have in view. Speyer (D.R.P., Arthur Speyer, 99570, November 2, 1897) produces an antiseptic which easily gives off CH_2O . For this purpose he uses naphthol or polyphenols like resorcin or pyrogallol and adds an excess of ammonia and of formaldehyde. This gives him an insoluble powder which easily liberates CH_2O and NH_3 . It is a well-known fact that ammonia reacts on formaldehyde and produces hexamethylenetetramine, $C_6H_{12}N_4$ (Wohl, *Ber.*, 1892, xix.; Tollens, *Ber.*, xvii., 653), which easily acts upon acids, and forms again CH_2O , NH_3 , and methylamine (see also Moschats and Tollens, *Ann. der Chemie*, cclxxii., 280).

Two recent patents relate directly to the manufacture of soluble fusible resins. One of Farbenfabriken Friedr. Bayer and Co. (D.R.P., Farbenfabriken vorm. Friedr. Bayer and Co., 201261, April 16, 1907) uses orthocresol so as to obtain an odourless shellac substitute.

The other issued to Grognot (L. Grognot, U.S.P., 391436, 1908), also for a shellac substitute, adds glycerin first, then after the reaction is over distils the solvent off.

After I had filed my own patent claims in the U.S., which gave me International Convention privileges, Helm (Engl. Pat., Louis Helm, 25216, November 13, 1907) described, after me, amines or ammonium salts as condensing agents for the manufacture of synthetic resins with phenols and formaldehyde. He does not clearly indicate the chemical or physical properties of his resins. He furthermore makes the rather ambiguous statement that ammonium nitrate can be used as well as aniline. I have shown (see *prox.*) that in the case of ammonium nitrate the end-product may be a fusible soluble resin, while in the case where aniline is used I obtain finally an insoluble infusible resin.

It is true that Helm uses large amounts of aniline and nitrate of ammonium; his indicated proportions are very close to molecular proportions, and this undoubtedly has, as I will show later, a great influence on the nature of the resulting products.

Knoll (Eng. Pat., Knoll and Co., 28009, December 19, 1907; Swiss Pat., ditto, 40994, December 7, 1907), who also applied for patents after the filing date of my U.S. patents, uses sodium sulphite or *neutral*, or *acid*, or *alkaline* salts as condensing agents; disregarding again the fact established by me, that according to whether an acid, a base, an acid salt, or an alkaline salt be used, the resinous products may be totally different.

This will close my review of the work done by others, and I shall begin the description of my own work by outlining certain facts, most of which seem to be unknown to others, or if they were known their importance seems to have escaped attention. Of these facts I have made the foundation of my technical processes.

As stated before, the condensation of phenols with formaldehyde can be made to give, according to conditions and proportions, two entirely different classes of resinous products. The first class includes the products of the type of Blumer, DeLaire, Thurlow, &c. These products are soluble in alcohol, acetone, or similar solvents, and in alkaline hydroxides. Heating simply melts them and they re-solidify after cooling. Melting and cooling can be repeated indefinitely, but further heating will not transform them into products of the second class. They are generally called "*shellac substitutes*," because they have some of the general physical properties of shellac.

The second class includes the products of Kleeberg, Smith, Luft, Story, Knoll, as well as my own product, in so far only as their general properties are concerned; but each one of them may be characterised by very distinct specific properties which have a considerable bearing on any technical applications. Broadly speaking, this second class can be described as infusible resinous substances, derived from phenols with aldehydes; some of them are more or less attacked by acetone, by caustic alkalis, or undergo softening by application of heat. At least one of them is unattacked by acetone, and does not soften even if heated at relatively high temperatures. None of them can be re-transformed into products of the first class even if heated with phenol.

These insoluble infusible substances can be produced directly in one operation by the action of formaldehyde on phenols under suitable conditions; for instance, the process of Kleeberg (see above). Or they may be produced in two phases (see Luft and Story above), the first phase consisting of an incomplete reaction giving a viscous product that is soluble in alcohols, glycerin, camphor, or phenol, and which on further heating or after driving off the solvent may gradually change into an infusible product.

In order to be able to stop at the first phase, the condensing agents may either be omitted (see Story above) or they may be used moderately (see Luft above) or they may be diluted with suitable solvents; for instance, methyl- and amyl-alcohol (see Smith above), or with glycerin (see Payolle above).

(To be continued).

NOTICES OF BOOKS.

Practical Agricultural Chemistry for Elementary Students.

By J. BERNARD COLEMAN, A.R.C.Sc., F.I.C., and FRANK T. ADDYMAN, B.Sc.(Lond.), F.I.C. New Edition. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1909.

THE student who is beginning a course of agricultural chemistry cannot do better than work through the practical work described in this book. It has been written for those who have previously learned no chemistry whatever, and gives first of all a description of the preparation and manipulation of apparatus which is to a certain extent an abstract of Prof. Coleman's larger work on practical chemistry. The preparation and properties of the gases of the atmosphere and of water are next treated, and methods of qualitative analysis as applied to manures, soils, feeding materials, and dairy produce are described in Section III. This section takes into consideration the special requirements of the agricultural student, and gives a good course of elementary practical work to accompany lectures on the constituents of feeding materials, manures, &c.; thus the student gets practice in simple experimental work, and at the same time can feel that he is adding to his know-

ledge of his special subject. The last section contains a short scheme of analysis for those metals and acid radicles which would be most likely to be met with in agricultural work, with some separation tables.

Laboratoriumsbuch für die Braunkohlenteer-Industrie. ("Laboratory Book for the Brown Coal Tar Industry"). By Dr. ED. GRAEFE. Halle-a-S.: Wilhelm Knapp. 1908.

THIS book is a companion volume to the monograph on the brown coal-tar industry written by the same author, and contains directions for the testing of the products obtained from tar in the laboratory. The book contains a good deal of information on practical methods, and the subject is treated really scientifically; for instance, the tests of the value of wax candles of different composition are thoroughly described and illustrated, and all the details for the investigation of wax, wick, &c., are explained fully. As a short guide to laboratory work the book is admirable, being concise and thoroughly practical, while, to the young chemist especially, the fact that it gives full directions for one method which has proved reliable for each determination, instead of a critical review of many, with perhaps a detailed account of none, is a great recommendation.

Dialyse, Eiweisschemie, und Immunität. ("Dialysis, The Chemistry of Albumens, and Immunity"). By R. P. VAN CALCAR. Leiden: S. C. van Doesburgh. Leipzig: Johann Ambrosius Barth. 1908.

AN interesting account of dialysis and its application to the study of biochemistry is given in this monograph. The author has a firm belief in the value of dialysis as a means of investigating biological products, and has some important results to report. In the first chapter a full account is given of the process, and different kinds of dialysers are described, with short directions for using them. Chapter II. gives a review of the biochemistry of the albumens, and goes shortly into the chemistry and composition of the most important representatives of these substances. The third chapter is devoted to a description of the results which have been obtained when blood serum is dialysed. The author's work has confirmed the fact that albumens which do not dialyse do not undergo putrefaction. Thus a solution impregnated with micro-organisms does not show any development of them during dialysis, and when the process is stopped they again begin to increase.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlviii., No. 10, March 8, 1909.

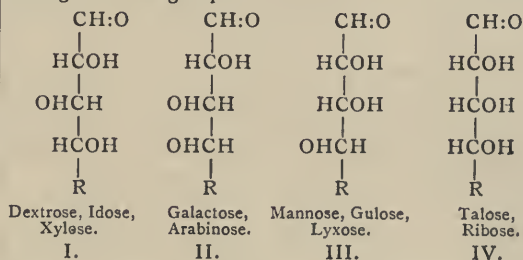
Spontaneous Crystallisation.—René Marcellin.—Experiments with lead acetate have shown that, other things being equal, the power of spontaneous crystallisation diminishes with the time during which the substance has been kept in the liquid state, but is independent of the number of crystallisations which divide up the total time of fusion. Moreover, other things being equal, the power of spontaneous crystallisation diminishes when the temperature at which the liquid has been kept is increased. The hypothesis of dust in suspension causing crystallisation is confirmed by the author's work, and in certain cases either with the naked eye or the microscope he has observed dust at the centres of crystallisation. The phenomenon of spontaneous crystallisation appears closely allied to that of the condensation of vapours.

Nature of Metatungstates. Rotatory Power of Crystals of Potassium Metatungstates.—H. Copaux.—When the ordinary alkaline tungstates $\text{WO}_3 \cdot \text{M}_2\text{O} + \text{Aq}$ are boiled with any acid, they are transformed into metatungstates to which the formula $(4\text{WO}_3)\text{M}_2\text{O} + \text{Aq}$ has been given. The author regards the metatungstates as complex tungstates in which the water is bound to the tungstic acid in an acid radical, so that it plays the same part as B_2O_3 , Si_2O_4 , and P_2O_5 in the boro, silico, and phosphotungstates. The formula he ascribes to them is $(3\text{H}_2\text{O} \cdot 24\text{WO}_3)6\text{M}_2\text{O} + \text{Aq}$. Various reactions which the metatungstates undergo appear to confirm this opinion. A hydrate $(4\text{WO}_3)\text{K}_2\text{O} + 6 \cdot 5\text{H}_2\text{O}$ is completely isomorphous with potassium borotungstate and potassium silicotungstate. Like these two salts it is dextro-rotatory.

Phosphides of Tin.—Pierre Jolibois.—Various phosphides of tin, of formulæ Sn_3P_2 , SnP , Sn_2P , SnP_2 , Sn_3P_2 , SnP_3 , have been described by different authors. The author has prepared a homogeneous specimen containing 16.5 per cent of phosphorus, and corresponding to the formula Sn_4P_3 . By allowing phosphorus to act upon tin under pressure, another definite compound is formed, and it may be isolated by the action of hydrochloric acid, soda, and nitric acid on the mixture obtained. Its formula is SnP_3 . This phosphide has already been described by Rose. There is no reason for believing in the existence of compounds of formulæ Sn_5P_2 , Sn_2P , Sn_3P_2 , SnP , SnP_2 .

Experiments with an old Glass which has been turned Violet by the Sun's Rays.—M. Delachanal.—By fusing a specimen of old violet glass in a vacuum the author has found that the occluded gas consists chiefly of a gas which is absorbed by potash; it also contains oxygen and a little nitrogen. The deposits obtained by sublimation consist of sodium chloride, sodium sulphate, potassium sulphate, and arsenic trioxide.

New Method of Determining the Constitution of Sugars.—M. Hanriot.—The chloraloses of different sugars give chloralic acids on oxidation. On examining the formulæ of these acids it will be seen that their isomerism can depend upon only three carbon atoms, namely, the three which are adjacent to the aldehyde group of the sugar. According to Fischer's formulæ the sugars can be arranged in four groups:—



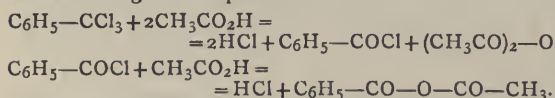
The three sugars of each group will give identical chloralic acids. This reaction provides a convenient method of determining the partial constitution of an unknown aldehydic sugar containing C_3 or C_6 . It is only necessary to make it combine with chloral, which is usually quite easy, and to isolate the chloralose. If this is identical with a known chloralose the sugar is determined, since every sugar has a different chloralose. If a new sugar is being investigated its chloralose must be oxidised to the acid, and then, according as this is a dextro, galacto, or manno acid, it may be deduced that the sugar belongs to the first, second, or third class. If a new acid is obtained it must belong to the fourth group, of which the author has not yet obtained a representative. Levulose gives a dibasic chloralic acid. Sorbose has not yet been made to yield a chloralose.

Importance of Temperature in Direct Decompositions.—Albert Colson.—Certain ether salts, chiefly benzoic ethers, when heated in sealed tubes, are unaltered

at a temperature of 290° , but decompose at 300° : $C_6H_5CO_2C_nH_{2n+1} = C_6H_5CO_2H + C_nH_{2n}$. Methyl benzoate yields only carbon dioxide at 350° , and hence behaves quite differently from its homologues. From the results of these experiments it appears that each substance has its own temperature and method of decomposition, which cannot always be foreseen. The principal factor is the temperature.

Transformation of Pinonic Acid into 1-3-Dimethyl-4-Phenylacetic Acid.—Ph. Barbier and V. Grignard.—By the action of bromine on pinonic acid a monobasic acid of formula $C_{10}H_{12}O_2$ is obtained. It is formed from pinonic acid according to the equation $C_{10}H_{16}O_3 = C_{10}H_{12}O_2 + H_2O + H_2$. From its reactions and its physical constants it is undoubtedly 1-3-dimethyl-4-phenylacetic acid. Hence an intramolecular change must take place in the pinonic acid, since the product has a constitution which differs greatly from the initial substance.

Preparation of Anhydrides of Cyclic and Acyclic Acids.—A. Béhal.—Benzo-trichloride reacts with acetic acid according to the equations—



Benzoyl chloride is formed as an intermediate product, but is rapidly decomposed in presence of acetic acid. Thus it is possible to obtain anhydrides of cyclic acids and the acids themselves from the trihalogen derivatives, and the same reaction may be applied to the anhydrides of acyclic acids and to the fatty acids.

MISCELLANEOUS.

Institute of Chemistry.—Pass List, March-April Examinations, 1909.—Of ten candidates who presented themselves for the Intermediate Examination, the following six passed: B. M. Brown, A. S. Dodd, F. S. Haines, G. S. W. Marlow, G. A. Smiley, B.Sc. (Lond.), and O. J. Stone. Two candidates presented themselves for the Final Associateship Examination in the Branch of Mineral Chemistry, and one passed: P. W. Copeland, B.Sc. (Lond.). In the Branch of Metallurgical Chemistry, of two examined one passed: H. T. Reeve. Of five candidates who presented themselves in the Branch of Organic Chemistry, the following three passed: C. Gilling, B.Sc. (Lond.), G. E. Johnson, B.Sc. (Lond.), and J. Yates, M.Sc. (Manc.), B.Sc. (Lond.). In the Examination in the Chemistry of Food and Drugs, and of Water, of six who presented themselves, four passed: T. Cockburn, C. E. C. Ferrey, P. A. W. Self, B.Sc. (Lond.), and F. F. Shelley. Three of the candidates, J. Yates, T. Cockburn, and F. F. Shelley, were examined for the Fellowship.

Seventh International Congress of Applied Chemistry, London, 1909.—Provisional Programme:—

Wednesday evening, May 26—Reception by the Lord Mayor and Corporation of the City of London at the Guildhall (levee, uniform, or evening dress).

Thursday, May 27—10 a.m., Meeting of the Joint Organising Committee; 3 p.m., Inaugural Meeting, opened by H.R.H. The Prince of Wales, in the Royal Albert Hall (morning dress); Evening, Reception by the Foreign Office (evening dress).

Friday, May 28—10 a.m. to 1.30 p.m., Sectional Meetings; 2.30 p.m., General Lectures by Professors Haller and Paterno; Evening, Banquet at the Crystal Palace (evening dress).

Saturday, May 29—10 a.m. to 2 p.m., Sectional Meetings; Afternoon, Garden Party at the Botanic Gardens by the Ladies' Committee; Evening, Reception

by the London Section of the Society of Chemical Industry at the University of London (evening dress). Monday, May 31—10 a.m. to 1.30 p.m., Sectional Meetings; 2.30 p.m., General Lecture by Prof. O. N. Witt; 4 to 6 p.m., Sectional Meetings; Evening, Private Receptions (evening dress).

Tuesday, June 1—10 a.m. to 1.30 p.m., Sectional Meetings; 2.30 p.m., General Lecture by Sir Boverton Redwood; 4 to 6 p.m., Sectional Meetings; Evening, Reception at the Natural History Museum (evening dress).

Wednesday, June 2—10 a.m., Official Closing Meeting of the Congress; Afternoon, Visit to Windsor Castle, by permission of the King.

In regard to the Banquet at the Crystal Palace—at which it is hoped all members will be present—special trains will be run, and every arrangement made for the convenience of members; the price for the Banquet ticket, £1 1s., includes the railway fare. In order that the extensive preparations for this large function be properly made, it is necessary to know the number of guests in good time. It is particularly requested therefore that applications for tickets be received not later than May 3rd. Tickets for guests who are not members of the Congress can be obtained, price 25s. each; ladies tickets, 21s. each. Special trains will convey members from Paddington Station to Windsor on Wednesday afternoon, June 2nd. All members of the Congress, and ladies accompanying them, are invited as guests. After April 19th the offices for the Congress will be transferred from Cromwell Crescent to the Royal College of Science, South Kensington, London, S.W.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Sea-water for Boilers.—(Reply to "Corrosion").—The trouble may be due to several causes; I do not think that HCl in the steam has anything to do with it. If the condenser tubes are pitted in isolated spots, or only a few tubes in a set, it is pretty certain to be due to specks of oxide of iron settling in the tube, when not in use, and starting electrolytic action. This form of the trouble is really due to a badly designed condenser; it may be minimised by swilling the tubes well after not being in use, and it is sometimes recommended to pass a wire brush through them to remove the scale. If the tubes corrode all over and not in isolated patches, it may be due to electrolysis caused by the electric installation. If this is not the case, it may be owing to the tubes being made of too pure an alloy; this may be avoided by specifying the alloy to contain about 0.25 per cent tin. The British Admiralty use the alloy of 70 per cent copper, 29 per cent zinc, and 1 per cent tin.—ERNEST A. LEWIS.

MEETINGS FOR THE WEEK.

MONDAY, 5th.—Royal Society of Arts, 8. (Cantor Lectures). "Aërial Flight," by F. W. Lancaster.

TUESDAY, 27th.—Royal Institution, 3. "The Brain in relation to Right-handedness and Speech," by Prof. F. W. Mott.

—Paraday Society, 8. "Experiments on the Current- and Energy-efficiencies of the Finlay Alkali Chlorine Cell," by F. G. Donnan, J. T. Barker, and B. P. Hill. "Coefficients of Absorption of Nitrogen and Oxygen in Distilled Water and Sea-water, and of Atmospheric Carbonic Acid in Sea-water," by C. J. J. Fox. "Electromotive Force of certain Platinum Compounds, with Special Reference to the Oxygen-hydrogen Gas Cell," by P. E. Spielmann.

WEDNESDAY, 28th.—Royal Society of Arts, 8. "The Resources of the Peruvian Andes and the Amazon," by C. R. Enoch, F.R.G.S.

THURSDAY, 29th.—Royal Institution, 3. "Aspects of Applied Aesthetics," by James Paterson, A.R.S.A.

—Royal Society of Arts, 4.30. "The Problem of Indian Labour Supply," by Selwyn Howe Fremantle, I.C.S.

FRIDAY, 30th.—Royal Institution, 9. "The Pitfalls of Biography," by Edmund Gosse, M.A.

SATURDAY, May 1st.—Royal Institution, 3. "The Earth Movements of the Italian Coast, and their Effects," by Robert T. Günther.

—Royal Institution, 5. Annual Meeting.

THE CHEMICAL NEWS.

VOL XCIX., No. 2579.

THE DISCOVERY OF BROMINE.

By F. D. CHATTAWAY, F.R.S.

OF all the halogens bromine has the least eventful history. Its relationship to chlorine and iodine was recognised from the first, and it took its position among the elements without challenge.

The discovery of bromine has, however, a peculiar interest of its own, since it was the work of a young man not yet twenty-four years of age, who by this, his first research, took at once a prominent place among the chemists of his time.

Bromine was discovered about 1826 by Antoine Jérôme Balard, who was at the time lecture assistant in the School of Pharmacy at Montpellier.

The incident which directed his attention to the mother-liquors left after salt had been crystallised out of the concentrated waters of the neighbouring salt marshes, is thus related by Wurtz* :—"About 1824, when botanising one spring morning near the edge of a salt marsh, Balard noticed a deposit of sodium sulphate, which the coolness of the night had caused to crystallise out in a basin where someone had left a quantity of mother-liquor after separating common salt. The idea of studying these mother-liquors immediately took possession of his mind and occupied it during the greater part of his life. In the course of his subsequent experiments he was struck by the peculiar coloration which certain reagents developed in such mother-liquors. He made the most of this observation, and following it up with a tenacity amounting to genius, he had the good fortune to discover bromine. It was a great discovery. Balard had isolated a new simple body, not an insignificant rare metal hidden in some little-known mineral, but a highly important substance destined to rank between chlorine, which we owe to Scheele, and iodine, which we owe to Gay-Lussac. Thus, the name of this young man of twenty-four was placed at the outset of his career by the side of these illustrious names, and there it has become immortal."

Balard published the account of his discovery in the *Annales de Chimie et de Physique* (1826, xxii., 327) under the title, "Sur une Substance particulière contenue dans l'eau de la mer." He commences with a short historical sketch :—

"I have many times noticed on treating the lye of sea-weed ash with an aqueous solution of chlorine after having added some starch paste, that not only did a blue zone due to iodine appear, but also a little above this a zone of a rather intense yellow colour. The latter was also observed when the mother-liquors of our salt works were treated in the same way, and the tint was deeper in proportion as the liquid was more concentrated. The appearance of this colour was accompanied by a particularly piercing odour.

I sought to discover what the nature of this colouring matter could be, and my first attempts led me to the following observations :—

1. The mother-liquor of the salt works thus treated with chlorine loses its characteristic colour and smell after one or two days' exposure to the air, and fresh chlorine is then no longer able to reproduce the same phenomenon.

2. The smell and colour alike disappear when the liquid is treated with alkalis or alkaline carbonates.

3. A similar effect is produced when to the coloured liquid is added any reagent able to yield hydrogen, either by itself or through the intervention of water. Such reagents are sulphurous acid, ammonia, and sulphuretted hydrogen, and especially zinc and sulphuric acid, which yield hydrogen in the nascent state.

4. When the decoloration has been effected by alkalis or by the agency of hydrogen, the addition of more chlorine causes the colour to appear anew.

Two interpretations naturally offer themselves as an explanation of these different phenomena. The yellow colouring matter may be regarded as a combination of chlorine with one of the materials contained in the mother-liquor of the salt works, or as a substance set free from one of its compounds by chlorine which had taken its place. In order to decide which explanation to adopt, it was indispensable to isolate the colouring matter. As its volatility seemed to promise that distillation would separate it from the liquid I had recourse to it. The yellow coloured liquid on being submitted to distillation liberated, at the first moment of boiling, very thick reddish coloured vapours which condensed on cooling to a liquid possessing most of the properties of the original coloured liquid, but in a much more pronounced degree.

The reddish liquid obtained had a smell comparable to that of the oxide of chlorine; it was destitute of acidity, and lost its colour when acted upon by alkalis, sulphurous acid, hydrogen sulphide, and so on; in a word, by all those agents which decolorised the mother-liquor of the salt works itself when reddened by chlorine. It could not therefore be doubted that the first product of distillation contained the substance with which I had to do, especially as the rest of the liquid had lost its former qualities, as its colour and penetrating odour had disappeared, and as chlorine was able no longer to give to it a yellow tint.

To obtain the red substance in a pure state it was only necessary to separate the water which had volatilised simultaneously with it.

To this end I passed the reddish vapours over chloride of calcium; they then condensed in a little receptacle in drops of a deep red colour which filled any vessel in which they were placed with a vapour similar in colour to nitrous fumes.

The yield of the colouring matter, which I now believed that I had obtained in a state of purity, was very small, and I regarded an operation as successful which gave me a single drop of the liquid. Such small quantities of material did not lend themselves to experiments of any magnitude. I was, however, able to make some conjectures as to the nature of the new substance, and the further researches which I have been able to carry out on a larger scale have confirmed them.

I was inclined at first to regard the substance as a chloride of iodine, though different from the compounds of this nature hitherto recognised by chemists.

It was, however, in vain that I essayed to establish the presence of iodine, its refusal to colour starch blue, and the white precipitate which it formed with the proto-nitrate of mercury and with nitrate of lead assured me that no iodine was contained in it.

On the other hand, I could not detect any indication of decomposition when it was submitted successively to the action of the voltaic pile and to a high temperature. Such a resistance to decomposition could not fail to suggest to me the idea that I had to deal with a simple body, or with one comporting itself as a simple body, and indeed I was confirmed in this view when I regarded the entire treatment to which I had subjected the substance.

I came, therefore, to the conclusion that I had found out a new simple substance closely resembling chlorine and iodine in its chemical aptitudes, and forming absolutely analogous compounds, but showing marked points of difference from them both in its physical properties and chemical behaviour, and clearly to be distinguished from them."

* In an oration which he proposed to deliver at the graveside on Balard's death in 1876. This, however, was not done in deference to a wish expressed by Balard himself, and the account of his life and work was afterwards published in the *Journal de Pharmacie et de Chimie*, 1876, xxiii., 375.

He next deals with the name to be given to the new substance.

"The view which I had adopted as to the nature of the red substance obtained from the water of the salt-works by the action of chlorine made it necessary to give to it a name by which it could be designated, a name which, while enabling such terms as 'red substances' and 'substance set free by chlorine' to be dispensed with, would indicate my view of its elementary nature, and which could also be utilised in naming its combinations. I turned to the learned professor under whom I had the honour of being a student . . . M. Anglada, and he advised me to call it *Brome*,* deriving the name from the Greek *βρωμος* (factor).† This name lends itself wonderfully well to the formation of the composite terms which its combinations necessitate, and I therefore adopt it. If other chemists confirm the results which I think I have reached, and place this new substance definitely among the elements, I am of opinion that this name can be retained."

Balard describes two procedures which he has successfully used for the extraction of bromine. In the first, the element is obtained by simply distilling the mother-liquor of the salt-works after treating it with chlorine. A little bromine is easily obtained in this way, but as it is never pure Balard abandoned the method in favour of another, in which it is not distilled off but is extracted by ether. The bromine is then removed from the ether by shaking it with a small quantity of potash. When a sufficient quantity of potassium bromide has been thus obtained it is re-crystallised, and the element is obtained from this purified material by distilling it with manganese dioxide and sulphuric acid, passing the bromine liberated into water, and subsequently separating it and drying it over calcium chloride.

Summing up the arguments in favour of its elementary nature, Balard concludes:—"A substance which in the free state resists as effectively as does bromine all attempts to decompose it, which is expelled by chlorine from all its compounds possessed of exactly its original properties, which when allowed to act on compounds containing iodine substitutes itself in every case for the latter element to play a similar part in the new products, and which, in spite of some differences of action, is connected with both chlorine and iodine by the most sustained analogies, seems to possess the same right to be considered as a simple body."

"If these results are confirmed by other chemists, bromine must as a simple body rank along with chlorine and iodine, and it is manifestly between these elements that it must be placed."

Battersea Polytechnic.—Technical Bacteriology.—Among the recent developments of the work of the Chemical Department of the Battersea Polytechnic has been the institution of a successful evening class in Technical Bacteriology, held during the session 1908-1909. At the end of the session an examination was held by an outside examiner (A. Harden, Esq., D.Sc., Ph.D.), appointed by the Polytechnic. Polytechnic certificates will be awarded to the following successful candidates:—First Class—Evelyn H. Shepherd, Russell G. Pelly. Second Class—Samuel Bell, James F. Rowland, Andre Bracher, Harry B. Willson, Percy W. Narracott. The candidates in each class are placed in order of merit.

* Altered in English into *Bromine* to bring it into harmony with the names used for the other halogens.

† A sentence in a short complimentary communication appended to Balard's paper by Vauquelin, Thenard, and Gay-Lussac, who were requested by the Academy to express their opinion upon it, seems to indicate that Balard originally proposed the name "muride" for the new substance, but abandoned it for the one now so familiar on their pointing out the various objections which could be made to it. They say:—"M. Balard gave the name muride to the new substance, but as many objections can be made to this denomination we have replaced it with the consent of the author by that of brome, from *βρωμος*—bad odour."

A NEW THEORY OF MOLECULAR VOLUMES.

By GERVAISE LE BAS, B.Sc.

(Continued from vol. xcvi., p. 88).

The Volume Relations in Closed-chain Compounds.

IN a former paper it was shown that the molecular volumes of the "open chain" hydrocarbons, saturated and unsaturated, can be calculated by means of the following formulæ:—

$$\left. \begin{array}{ll} \text{Saturated paraffins} & \dots C_n H_{2n+2} = (6n+2)S \\ \text{Olefines} & \dots C_n H_{2n} = 6nS \\ \text{Acetylenes} & \dots C_n H_{2n-2} = (6n-2)S \end{array} \right\} WS$$

W represents the number of valencies, S is a number approximately constant, and equal to 3.70 at the boiling-point and 9.67 at the critical-point.

The magnitude of S is equal to H.

Volume Relations in Hydrocarbon Side-chains.

From the fact that the constitution of hydrocarbon side-chains is similar to that of hydrocarbons in the fatty series, it might be expected that there should also be a similarity in the volumes of like atoms. This is found to be so, because the differences which represent the volumes of the homologous increment, CH_2 , have been shown by Schiff to be equal to about 22, which is normal.

TABLE IX.—The Volumes of the Side-chains in Monocyclic Compounds.

Compound.	V.	nCH_2 .	CH_2 .
Benzene, C_6H_6	96	22	
Toluene, $C_6H_5-CH_3$	118.3	22.3	22.30
Xylene, $C_6H_4-(CH_3)_2$	140.3	44.3	22.15
Mesitylene, $C_6H_3-(CH_3)_3$	162.8	66.8	22.26
Cymene, $C_6H_4<\begin{smallmatrix} CH_3 \\ C_3H_7 \end{smallmatrix}$	184.9	88.9	22.22
Pyridene, C_5H_5N	89.3		
Picolene, $C_5H_4N-CH_3$	111.5	22.2	22.20
Hexahydrotoluene, $C_6H_{11}-CH_3$	141.8		
Hexahydroxylene, $C_6H_{10}-(CH_3)_2$	164.3	22.5	22.50
Mean value of CH_2		22.27	

The following data show that the volumes of CH_2 are the same in the side-chains of aromatic compounds as in straight-chain compounds, and that thus the volumes of C and H are also the same. Note also the following:—

M.V. of methyl phenyl propionate, $C_{10}H_{12}O_2$,— $C_6H_5.CH_2.CH_2.COOCH_3$	196.0
M.V. of methyl cinnamate, $C_{10}H_{10}O_2$,— $C_6H_5.CH=CH.COOCH_3$	188.6
Volume of H_2	7.4
M.V. of methyl cinnamate, $C_{10}H_{10}O_2$,— $C_6H_5.CH=CH.COOCH_3$	188.6
M.V. of ethyl benzoate, $C_9H_{10}O_2$,— $C_6H_5.COOC_2H_5$	174.4
Volume of C	14.2

It is also interesting to calculate the value of the "extra hydrogens" in hydroaromatic compounds, by subtracting from their molecular volumes the values for the corresponding aromatic derivatives. (See Table X.).

The value of H in the unsubstituted compounds seems to be a little below the normal at the boiling-point, and, in the substituted compounds, slightly above it. It is remarkable also that the unsaturated part of naphthyl hydride has the same effect as side-chains.

TABLE X.—Showing the Volume of H_6 in Hydroaromatic Compounds.

Compound.	V.	6H.	H.
Benzene, C_6H_6	96		
Hexamethylene, C_6H_{12}	116.3	20.3	3.38
Pyridene, C_5H_5N	89.3		
Piperidine, $C_5H_{11}N$	108.8	19.5	3.25
Toluene, C_7H_8	118.3		
Hexahydrotoluene, C_7H_{14}	142.1	23.8	3.97
Xylene, C_8H_{10}	140.3		
Hexahydroxylene, C_8H_{16}	164.3	24.0	4.00
Naphthalene, $C_{10}H_8$	147.2		
Naphthyl hydride, $C_{10}H_{14}$	171.2	24.0	4.00

There is strong evidence—to be immediately given—that all the hydrogen atoms in benzene, C_6H_6 , and hexamethylene, C_6H_{12} , have the same volume. It will be further seen that $C=4H$, and also in those compounds which possess a nitrogen atom in the nucleus—as pyridene, C_5H_5N , $N=3H$.

The result is to make the volumes of the above compounds still proportional to their valency numbers.

TABLE XI.—Showing the Values of V/W for a Number of Cyclic Compounds.

Compound.	$V_{B.P.}$	W.	V/W	V_K	W.	V/W
Benzene, C_6H_6	96	30	3.20	256.3	30	8.54
Hexahydrobenzene, C_6H_{12}	116.3	36	3.23	306.7	36	8.52
Pyridene, C_5H_5N	89.3	28	3.19	$\Delta = 50.4$ for H_6		
Piperidine, $C_5H_{11}N$	108.8	34	3.20	$H=8.40$		
Paraffins			3.70			9.67

A more minute examination of C_6H_6 and C_6H_{12} is possible, owing to some accurate data given by Young (*Trans. Chem. Soc.*, 1889). The compounds in question are examined under identically reduced pressures.

TABLE XII.—Relation between the Molecular Volumes of Benzene, C_6H_6 , and Hexamethylene, C_6H_{12} .

ρ/ρ_K	C_6H_{12}	W=36.	C_6H_6	W=30.
	V.	V/W	V.	V/W
1.00000	306.7	8.52	256.3	8.54
0.82568	191.74	5.32	160.19	5.34
0.44232	153.27	4.26	127.12	4.24
0.14744	130.89	3.64	108.49	3.61
0.044232	119.82	3.33	99.19	3.30
0.022411	115.85	3.22	95.91	3.20
0.011797	112.97	3.14	93.50	3.12
0.001474	106.30	2.95	87.86	2.93

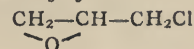
While the values of V/W in the two compounds are not quite identical, they are sufficiently close to indicate the existence of a similarity of structure in benzene and hexamethylene, and at the same time to furnish valuable evidence in favour of conclusion (b) at the end of the paper. It follows that a molecule swells or shrinks as it changes its structure, this swelling or shrinking being due to the change of volume of the individual atoms. It must, however, be observed that molecules may sometimes be heterogeneous as regards volume—a result which is due to the occurrence of differences in constitution in different parts of the same molecule. A carbon atom in the nucleus has not, for instance, the same volume as a carbon atom in a side-chain. Rule b is therefore limited in some respects, but these limitations can be usually ascertained from a knowledge of the chemical constitution of a molecule.

It will be gathered from the above that the nucleus as a whole has a smaller volume than that of a similar complex in the straight-chain series—a fact apparent in all compounds containing an aromatic or other nucleus. Kopp, indeed, was aware of some such effect, but it was not considered in his theory. Certain direct observations show

unmistakeably that this is the case. It will be our endeavour to demonstrate, by as direct methods as possible, that the diminutions, which can be more or less directly proved to be real, and can be accounted for by assuming that the relative volumes of the atoms are preserved, although their actual volumes change. The contractions found in the second case—and which are so far theoretical in that they are based upon an assumption given above—are equal to the contractions more or less directly observed. Thus it is ascertained that contractions found to exist in some cases of ring structure are characteristic of those types of structure; and, secondly, such total contractions are referred to diminutions in the individual atomic volumes.

Only direct observations will be considered in this paper in order to show the great importance of the above constitutive effect, and in order to demonstrate its value as one of the criteria of chemical structure. It will be of interest to consider the chemical compounds in the order of their complexity.

1. Epichlorhydrin, C_3H_5ClO ,—



$$\text{M.V. of } C_3H_5ClO \text{ (theoretical)} = 3 \times 14.8 + 5 \times 3.7 + 22.2 + 7.4 \quad \dots = 92.5$$

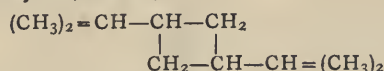
$$\text{M.V. of acetyl chloride, } C_2H_3O'Cl + CH_2-O'' + O' = 74.2 + 22.2 - 11.1 + 7.4 \quad \dots = 92.7$$

$$\text{M.V. of epichlorhydrin, } C_3H_5ClO \quad \dots = 87.5$$

$$\text{Difference} \quad \dots = -5.2$$

Cl possesses a volume of about 22.2 at the boiling-point, and oxygen 7.4 and 11.1, according to circumstances.

2. Diamylene, $C_{10}H_{20}$,—

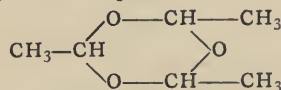


$$2 \text{ vols. of amylene, } C_5H_{10}, 2 \times 110.1 \quad \dots = 220.2$$

$$\text{M.V. of diamylene, } C_{10}H_{20} \quad \dots = 211.7$$

$$\text{Difference} \quad \dots = -8.5$$

3. Paraldehyde, $C_6H_{12}O_3$,—

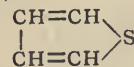


$$3 \text{ vols. of aldehyde, } C_2H_4O = 3 \times 56.7 \quad \dots = 170.1$$

$$\text{M.V. of paraldehyde, } C_6H_{12}O_3 \quad \dots = 151.0$$

$$\text{Difference} \quad \dots = -19.1$$

4. Thiophene, C_4H_4S ,—



$$\text{M.V. of dimethyl sulphide, } C_2H_6S \quad \dots = 75.1$$

$$\text{Add } 2CH_2 \quad \dots = 44.4$$

$$C_4H_{10}S \quad \dots = 119.5$$

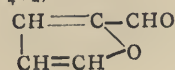
$$\text{Less } 6H \quad \dots = 22.2$$

$$C_4H_4S \quad \dots = 97.3$$

$$\text{M.V. of thiophene, } C_4H_4S \quad \dots = 84.9$$

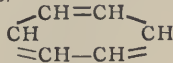
$$\text{Difference} \quad \dots = -12.4$$

5. Furfural, $C_5H_4O_2$,—

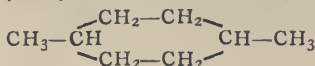


M.V. of propyl acetate, $C_5H_{10}O_2$	128.56
M.V. of caproic acid, $C_5H_{10}O_2$	130.00
Mean for $C_5H_{10}O_2$	129.28
Less 6H	22.20
$C_5H_4O_2$	107.08
M.V. of furfural, $C_5H_4O_2$	95.5
Difference	-11.58

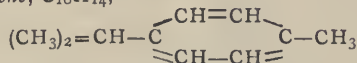
The following cases illustrate the types of ring structure belonging to aromatic, hydroaromatic, and allied compounds, including terpenes, but all possessed of a single six-membered ring:—

6. Benzene, C_6H_6 ,—

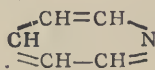
M.V. of diallyl, C_6H_{10}	126.1
Less 4H = 4×3.7	14.8
C_6H_6	111.3
M.V. of benzene, C_6H_6	96.0
Difference	-15.3

7. p-Hexahydroxylene, C_8H_{16} ,—

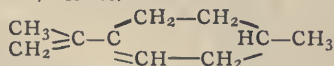
M.V. of octylene, C_8H_{16}	177.6
M.V. of hexahydroxylene, C_8H_{16}	164.3
Difference	-13.3

8. Cymene, $C_{10}H_{14}$,—

2 vols. of isoprene, $2(C_5H_8)$	207.8
Less 2H	7.4
$C_{10}H_{14}$	200.4
M.V. of cymene, $C_{10}H_{14}$	184.4
Difference	-16.0

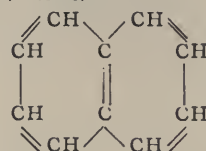
9. Pyridene, C_5H_5N ,—

M.V. of isoprene, C_5H_8	103.9
Less 3H	11.1
C_5H_5	92.8
Add N = 3H	11.1
C_5H_5N	103.9
M.V. of pyridine, C_5H_5N	89.3
Difference	-14.6

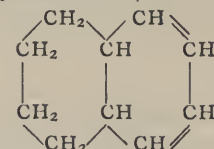
10. Carvene, $C_{10}H_{16}$,—

2 vols. of isoprene, $2C_5H_8 = C_{10}H_{16}$	207.8
M.V. of carvene, $C_{10}H_{16}$	190.3
Difference	-17.5

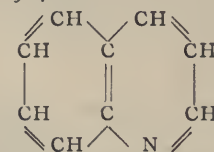
The following compounds, including two compounds (borneol and camphor) which possess bridged-rings, are remarkable in possessing double ring structure.

11. Naphthalene, $C_{10}H_8$,—

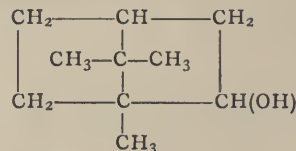
2 vols. of isoprene, $C_{10}H_{16} - H_2 =$	207.8 - 7.4	200.4
Less 6H		22.2
$C_{10}H_8$		178.2
M.V. of naphthalene, $C_{10}H_8$		147.2
Difference		-31.0

12. Naphthyl hydride, $C_{10}H_{14}$,—

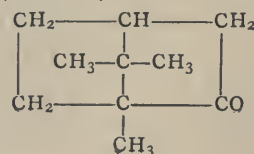
2 vols. of isoprene, $C_{10}H_{16} - H_2 =$	207.8 - 7.4	200.4
M.V. of naphthyl hydride, $C_{10}H_{14}$		171.2
Difference		-29.2

13. Quinoline, C_9H_7N ,—

Volume of $C_{10}H_8$ (see Naphthalene)	178.2
Less CH = $14.8 + 3.7$	18.5
C_9H_7	159.7
Or vol. of $C_9H_7 = 43 \times 3.7$	159.1
Add N = 3H	11.1
C_9H_7N	170.2
M.V. of quinoline, C_9H_7N	139.8
Difference	-30.4

14. Borneol, $C_{10}H_{18}O$,—

2 vols. of amylene, $2 \times C_5H_{10} = C_{10}H_{20}$, = 2×110.1	220.2
M.V. of octyl alcohol, $C_8H_{18}O$	190.8
Add 2C = 2×14.8	29.6
$C_{10}H_{18}O$	220.4
M.V. of borneol, $C_{10}H_{18}O$	190.5
Difference	-29.9

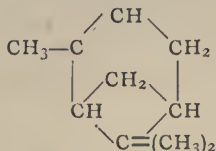
15. Camphor, $C_{10}H_{16}O$,—

2 vols. of isoprene, $C_{10}H_{16} = 2 \times 103.9$..	207.8
$O'' = 3H = 3 \times 3.7$	11.1
$C_{10}H_{16}O$	218.9
M.V. of camphor, $C_{10}H_{16}O$	187.4
Difference	-31.5

16. *Pinene*, $C_{10}H_{16}$.—A last compound of the terpene class is *pinene*, $C_{10}H_{16}$. Schiff (*Gazz. Chem. Italiana*, xiii., 177) gave the molecular volume of a terpene, $C_{10}H_{16}$, with a boiling-point of 156.1, which is probably pinene, M.V. 183.2.

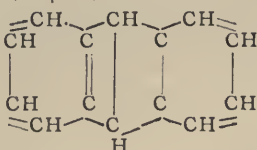
2 vols. of isoprene, $C_{10}H_{16}$, 2×103.9 ..	207.8
M.V. of pinene, $C_{10}H_{16}$	183.2
Difference	-24.6

This difference corresponds with Wagner's formula for pinene,—



which contains a picean ring. The two methyl groups are on the outside of the ring instead of inside as in camphene. They are of the nature of side-chains, and consequently do not partake of the contraction. Thus the contraction is -24.5 instead of -30, as in borneol, and no doubt in camphene.

17. *Anthracene*, $C_{14}H_{10}$.—



2 vols. of heptylene, $2(C_7H_{14}) = C_{14}H_{28}$ $= 2 \times 154.8$	309.6
Less $18H = 3 \times 22.2$	66.6
$C_{14}H_{10}$	243.0
M.V. of anthracene, $C_{14}H_{10}$	195.5
Difference	-47.5

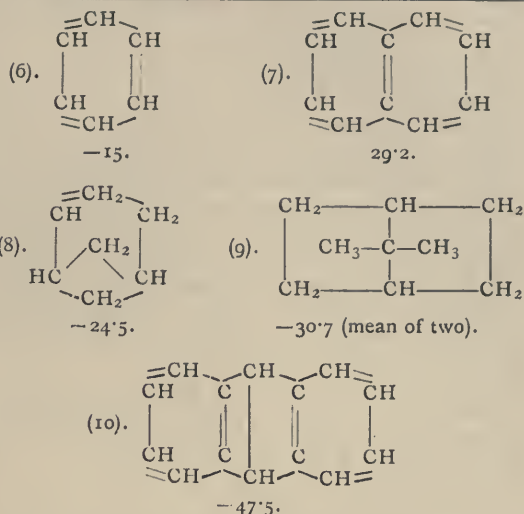
The above results are extremely interesting, and show that there is always a contraction when the type of structure changes from an "open-chain" to a closed-chain one.

The following is the amount of the contractions connected with the different types of rings:—

(1). $\begin{array}{c} CH_2 \\ \\ CH_2 \end{array} \begin{array}{c} \diagup \\ O \\ \diagdown \end{array}$ -5.	(2). $\begin{array}{c} CH_2-CH_2 \\ \quad \\ CH_2-CH_2 \end{array}$ -8.5.	(3). $\begin{array}{c} CH=CH \\ \quad \\ CH=CH \end{array} \begin{array}{c} \diagup \\ S \\ \diagdown \end{array}$ -12.4.
(4). $\begin{array}{c} CH=CH \\ \quad \\ CH=CH \end{array} \begin{array}{c} \diagup \\ O \\ \diagdown \end{array}$ -11.6.	(5). $\begin{array}{c} CH_2 \quad O-CH_2 \\ \quad \\ O-CH_2 \end{array}$ -19.1.	

The following are the contractions connected with well known types of structure:—

Empirical formula.	Aliphatic.	Δ .	(6) Aromatic or terpene.	Δ .	(7) Naphthalene.	Δ .	(8) Anthracene.
C_6H_{12}	132.4	14.2	118.2				
C_8H_{16}	177.6	13.3	164.3				
$C_{10}H_{14}$	200.4	16.0	184.4	29.2	171.2		
$C_{10}H_{16}$	207.8	17.5	190.3				
$C_{14}H_{28}$	309.6	13.8	295.8	29.2	280.4	47.5	262.1
Mean diff. . .	15.0			29.2		47.5	



The conclusion, which is also stated in Generalisation IV. (CHEMICAL NEWS, xcvi., 86), is that:—

(a) When the type of structure of a chemical compound changes from a straight-chain to that of a ring, the molecular volumes always contract, and this contraction increases as the number of members of single rings increase, and as the rings become more complex. The contractions are about the same for rings of similar types.

(b) The above contractions are apparently due to the diminished atomic volumes of the individual atoms. These, however, as a rule, maintain their characteristic relative volumes after the above change.

(c) In cases of mixed types of structure, however, the atomic volumes are respectively those characteristic of each type.

The great practical interest of these conclusions need scarcely be insisted on.

(To be continued).

AN ACCOUNT OF THE INFLUENCE OF HIGH POTENTIAL DISCHARGE ON AMORPHOUS GOLD.

By BAYARD G. COBB.

This account is the work of the writer during the months February to August, 1907, and was undertaken as a sequence to some work on radio-activity.

A quantity of amorphous gold was precipitated from a solution of $AuCl_3$ by $FeSO_4$, washed thoroughly many times with water and then with HNO_3 , finally with distilled water, every precaution being taken to obtain an absolutely pure product.

A quantity of the amorphous element, some 2 or 3 grms., was then taken and placed in a tube about 6 inches long and 1 inch in diameter (see Fig.), furnished with rubber



corks carrying electrodes, terminating in a flat plate (circular), and being connected to the terminals of the high tension (secondary) windings of a 10-inch Rhumkorf coil.

A current was then passed, and a spark discharged allowed to take place in the tube containing the gold for

the space of half an hour, at the end of which time the amorphous element was withdrawn and examined.

Some of the material immediately after the experiment was placed in close proximity to a plate (photographic) contained in a holder, and taken from a newly opened packet.

Some twenty minutes were allowed to elapse, and the plate was then submitted to the action of a developer, with the result that it appeared fogged. This action, resembling the effect produced by X-rays on photographic plates, appears, in the case of amorphous gold after being exposed as in this experiment, to wear off somewhat rapidly; as on the following day some of the gold treated was placed in proximity to a plate with hardly any appreciable effect, although the length of exposure in this second instance was very nearly doubled. In itself the gold after exposure appeared unchanged.

A quantity of the material was dissolved in aqua regia forming the chloride, was neutralised, and analysed in the ordinary way; this analysis, however, showing indisputably the presence of *copper*. The experiment has been repeated four times, with similar result every time.

Another tube was then fitted up, this time, however, being provided with the means of rendering the same partially vacuous. On the passage of the current for three-quarters of an hour, subsequent solution, and analysis, the presence of a copper salt was shown in even more marked degree. In every instance the electrodes employed were of pure platinum.

It may be that the effect of the high tension, high frequency current (for the Rhumkorf coil produces currents of three sorts) has caused some rearrangement of electrons or corpuscles forming the element gold; possibly some arrival at a change, perhaps, of position or complexity of the corpuscles.

Further experiments on this subject are now being done by the writer, which he hopes to chronicle at a later date.

Dawson City, Yukon Ty., Canada.

THE DECOMPOSITION OF WATER BY RADIUM SALTS.

By A. DEBIERNE.

RAMSAY has published much information on the decomposition of water by radium salts, which was first observed by Giesel. Thus he has shown that the composition of the gas spontaneously set free by a solution of a radium salt does not correspond to the formula $H_2 + O$, but that there is an excess of hydrogen; he observed the same decomposition by the action of the emanation on water, and stated also that the penetrating rays of radium do not produce the decomposition. Finally, in a recent communication (*Nature*, December, 1908), Ramsay mentioned that a solution containing a relatively large amount of radium bromide had nearly entirely ceased to set free the mixture of hydrogen and oxygen; yet this same solution had for a very long time previously regularly liberated the gases.

I had several times observed the decomposition of the water of a solution of a radium salt, and I had never noticed an anomaly such as that described by Ramsay, nor even an important diminution in the gas set free.

For example, in 1905 I observed the same solution of radium bromide for more than six months, and the volume of the gas varied from 0.385 to 0.378 cc. per day. During the same period a solution of actinium set free quantities varying from 0.171 to 0.170 cc. per day.

Moreover, during the last few months I have been observing a solution containing a large proportion of radium chloride, and up to the present I have obtained a regular liberation of 2.3 to 2.4 cc. a day. This would correspond on an average to 13 cc. per day for a gram of radium.

Ramsay suggests as the possible cause of the cessation

of the evolution of gas a spontaneous change in the properties of the radium.

Such a rapid change of properties is improbable, but it is not impossible to explain by secondary phenomena a diminution in the volume of gas set free in a solution of a radium salt. The fact, pointed out by Ramsay, that there is an excess of hydrogen in the gas proves that some of the oxygen is absorbed by the solution, and hence oxygenated compounds must be formed. These compounds may accumulate in the solution and cause the absorption of hydrogen at the moment of its formation. Thus the liberation of gas would be considerably diminished.

However, in spite of a great number of experiments dealing with the decomposition of water by radium it must be noted that Ramsay's last observation is unique, and also that the cessation of the evolution of gas occurred abruptly and unexpectedly in two or three weeks. Hence, I think that in Ramsay's last experiments there must have been some special circumstance which has escaped observation.

The decomposition of water in a solution of radium salt might be attributed either to the direct action of the radium or the emanation or their transformation products, or else to the action of the different radiations they emit—the α -, β -, or γ -rays.

This last action appears the most probable. As a matter of fact, in contradiction to Ramsay's statements, I have succeeded in effecting the decomposition of water without allowing contact between the water and the salt or emanation, simply by the action of the penetrating β - and γ -rays.

(NOTE.—I have already very briefly reported this result in a lecture delivered on April 4, 1908, before the Chemical Society of France, and published in June, 1908, in the *Bulletin* of this Society).

The experiment was arranged as follows:—A sealed glass tube containing a considerable amount of pure radium chloride was placed in a glass tube immersed in distilled water. The vessel containing the distilled water, which communicated with a mercury manometer, was completely exhausted. The rays acting on the water had already passed through the glass of the two tubes, *i.e.*, through a thickness of about 0.5 mm. The thickness of water round the tube was 12 mm.

The increase of pressure shown by the manometer was perfectly regular, and nearly exactly proportional to the time. In an experiment which lasted several months, however, I observed towards the end of the time a slight progressive diminution of the gas evolved. The evolution stopped altogether when the radium tube was removed. The gas obtained was completely absorbed by heated copper and copper oxide and phosphorus pentoxide. The volume was on an average 0.115 cc. a day per gram of radium.

In this experiment the energy necessary for the decomposition could only be obtained from the radiation absorbed by the water. This energy represents approximately the ten-thousandth part of the total energy set free by the radium, if it is assumed that the gas evolved has the composition $H_2 + O$. However, as the α -rays are entirely absorbed by the glass, and also a considerable proportion of the β -rays, it may be supposed that the energy absorbed by the water is only 1 per cent of the total energy. Hence it follows that about 1 per cent of the energy of the radiation absorbed by the water is transformed into chemical energy.

In the solution of radium chloride evolving 13 cc. of gas per day per gram of radium, the energy used for the decomposition is about 1 per cent of the total energy. If, adopting Ramsay and Cameron's statements, the proportion of energy used in the decomposition of water by the emanation is calculated, a much higher value is obtained.

Moreover, if the decomposition is due only to the action of the different kinds of rays, the quantity of gas disengaged would depend essentially on the proportion of the rays absorbed by the water.

Mdme. Curie was kind enough to lend me the radium which was used for these experiments.—*Comptes Rendus*, cxlviii., 703.

CHEMICAL ACTION OF THE PENETRATING RAYS OF RADIUM ON WATER.

By MIROSLAW KERNBAUM.

IN a recent note (*Comptes Rendus*, cxlviii., 703) Debiere has described the decomposition of water by the β - and γ -rays of radium, when there is no contact between the active salt and the water.

I have studied the composition of the gas produced by the action of these rays, so as to ascertain whether the proportion of oxygen to hydrogen is normal in this phenomenon, or if there is an excess of hydrogen, as Sir W. Ramsay has frequently observed in his experiments on the decomposition of water by radium emanation.

For these experiments M^{me}. Curie, in whose laboratory they were performed, was kind enough to place at my disposal a preparation of 100 mgrms. of nearly pure radium chloride. The salt was contained in a tube of thin glass, and the rays passed through this glass, some mm. of air, and the thin glass wall of the vessel containing the distilled water. The action of the α -rays was thus completely eliminated.

The water used in the experiment was previously boiled and introduced into the vessel exhausted to a pressure of 1/200 mm., and every precaution was taken to reduce to a minimum the amount of air in the apparatus.

The formation of a gaseous product was not shown by the mercury manometer until three days after the introduction of the radium into the inner tube of the vessel containing the water. I suppose that the liberation of gas began immediately, but did not exert any pressure on the column of mercury until the water, the volume of which was about a decilitre, was saturated.

After a month the radium tube was removed from the apparatus, and the gases which had collected above the surface of the water were removed into a graduated eudiometer tube which was provided with electrodes of platinum wire.

The volume of these gases measured under atmospheric pressure was about 200 cubic mm. When an electric spark was passed between the electrodes of the eudiometer under reduced pressure, only a very small diminution in the gaseous residue was observed. But after a certain amount of air had been introduced into the eudiometer tube, the passage of the spark caused a diminution in volume, such as could only be explained by supposing that the gas obtained was composed almost entirely of hydrogen.

Special care was taken to prevent the gases coming in contact with the grease of the stopcocks during these experiments, and before the commencement the apparatus was thoroughly washed with absolute alcohol and ether, in order to avoid any possibility of the absorption of oxygen. I therefore began to try to find out what had become of the oxygen.

When I tested with potassium iodide and a very dilute starch solution the water removed from the apparatus, I found hydrogen peroxide present in an amount which even exceeded the calculated quantity.

More exact experiments are in course of progression. For the present the results of this preliminary experiment may be summarised as follows:—The penetrating rays of radium when they act on distilled water through glass set free hydrogen, and simultaneously form hydrogen peroxide. *Comptes Rendus*, cxlviii., 705.

Royal Institution.—On Tuesday next, May 4, at 3 o'clock, Prof. Svante Arrhenius, Director of the Nobel Institute of Physical Chemistry, Stockholm, begins a course of two lectures on "Cosmogonical Questions" (these are the Tyndall Lectures); on Saturday, May 8, Prof. Walter Raleigh delivers the first of two lectures on (1) "Edmund Burke," (2) "Burke's Prose." The Friday Evening Discourse on May 7 will be delivered by Major Ronald Foss on "The Campaign against Malaria," and on May 14 by Prof. George E. Hale on "Solar Vortices and Magnetic Fields."

THE FRUIT OF THE *ARALIA HISPIDA*.

By J. MILTON GILCHRIST.

THE fruit of *Aralia hispida* was gathered at Sylvan Beach, New York, August 19, 1907. In certain areas of that territory it seems to grow very abundantly. It was dried in an oven at 105° to 110°, and while drying it had quite markedly the odour of thoroughwort (*Eupatorium*). The fruits were entirely ripe, and appear like juicy berries. They are dark blue or black in colour, and dark brown when dry and quite thick. Each berry has five arms like a star. The inside is hard, and each arm contains a relatively large nutlet of an oily appearance. The fruits have a slightly bitter taste, but in other respects the taste resembles that of currants. Each fruit weighs about 0.04 of a gram. There were 431 grms. of the dried berries available for this investigation. When a berry was enveloped in a clean platinum wire and held in the Bunsen flame, both the colours of sodium and potassium were distinctly visible.

The Sugars.

We placed 100 grms. of the fruit in a 500 cc. flask, and treated it with 95° alcohol. The flask was placed in a water-bath, and the contents gently boiled with a small flame. Each day we would pour off the alcohol extract and add a fresh portion of alcohol. This was continued for several days. Then we substituted for the alcohol distilled water, which seemed to extract the sugar more rapidly; yet thirty days were necessary for its complete removal. The filtrate finally became colourless, when at first it was of a deep brown colour. The clear filtrate gave no reaction with Fehling's solution. The extract contained some sediment, which was filtered off, and the filtrate was diluted to a volume of 515 cc. It had the odour of blackberry brandy, due no doubt to fermentation. Four-tenths of a centimetre was added to 50 cc. of distilled water; this was heated to boiling and titrated with Fehling's solution, of which 10 cc. corresponded to 0.05 gram sugar. The fruit was thereby shown to contain 41.72 per cent of sugar, which corresponded fairly well with the loss in weight of the original fruit.

A portion of the filtrate containing the sugars was digested for twenty-four hours on the water-bath with a relatively large amount of purified bone-black. The bone-black was removed by filtration, and some of the filtrate was evaporated on the water-bath to constant volume. A thick syrupy residue with only a slight tinge of yellow remained. We weighed out 0.2 gram of this residue, and treated it with phenyl-hydrazine and sodium acetate according to Sherman and Williams (*Journ. Am. Chem. Soc.*, xxviii., 629, May, 1906). The time of the osazone formation was one and a half minutes, which corresponds to fructose. We repeated this several times, always with the same result. The osazone was filtered off, and numerous attempts were made to crystallise it from alcohol, but there was no satisfactory result.

The Acids.

The alcohol-water extract reacted acid. The filtrate from the bone-black gave satisfactory tests for tartaric and citric acids, likewise acetic acid. The last, however, doubtless resulted from fermentation.

The Ash.

Four portions of berries were weighed out into a platinum dish and carefully heated until all or nearly all of the organic matter was consumed and only the ashes remained. While burning they had the odour of roasted coffee. The ash was dark grey in colour. From one portion, the silica, iron, aluminium, calcium, and magnesium were determined; from another portion, the alkalis; from another portion, the sulphate; and lastly, the phosphate. For the first portion we took 2.004 grms. of the berries and received 0.1838 gram of ash, or 9.12 per cent. The

usual amount was between 4 and 5 per cent. The results of the analyses were as follows:—

	Per cent of the ash.
SiO ₂	13.59
Fe ₂ O ₃	9.13
Al ₂ O ₃	9.13
CaO	1.25
MgO	1.72
Na ₂ O	25.66
K ₂ O	13.63
P ₂ O ₅	15.01
SO ₃	5.28
Total	94.40

There was a small quantity of CO₂ and unburned organic matter in each case which was not determined.

The Nitrogen.

This was determined by the Kjeldahl method. We weighed out 1.2093 grms. of the crushed fruits, which we heated with pure concentrated sulphuric acid until the solution became colourless. We obtained 1.5 per cent of nitrogen. It is the belief in some circles that the berries are poisonous. If so the poison would doubtless be one of the alkaloid poisons, but we received no precipitate with a solution of iodine in potassium iodide. If the nitrogen does not represent albumen it may be part of an amino group.

The Oils.

In order to have a larger quantity of the nutlets from which to extract the oils we removed the sugar and colouring matter from another 200 grms. of the fruits. We accomplished this quite rapidly by using a litre flask and large portions of alcohol and water. The nutlets were separated from the husks and thoroughly dried in the oven. We thus obtained 53 grms. from the 300 grms. of fruit. These were very hard and could not be pulverised in a heavy iron mortar, but we finally reduced them to a fine powder by using a coffee grinder.

The crushed nutlets were placed in a 500 cc. flask, which was connected with an inverted condenser and treated with successive portions of ether. The ether extract was removed each day and a fresh portion added. Three weeks were required to extract all the oils. The oils had a greenish colour, apparently from chlorophyll. They were digested in bone-black and distilled water for twenty-four hours, when the colour was entirely removed. There were 23.9663 grms., or 7.98 per cent of the original fruit, and about 45 per cent of the dried nutlets.

The oils were saponified by Koettstorfer's process. We weighed out 2.5346 grms. in a flask connected with a long vertical tube. We added 25 cc. of a normal solution of NaOH, and the same amount of alcohol. This was kept an hour and a-half in a boiling water-bath, when a complete solution of the fat took place. Phenolphthalein solution was added, and the alkaline solution was titrated with normal hydrochloric acid. The saponification equivalent was thus found to be 517, which corresponds to a palmitate.

Separation of the Saponification Products.

We placed 2.5 grms. of the oil in a 120 cc. flask, and saponified this with the alkali alcoholic solution. We added distilled water to the flask and acidulated the solution with dilute sulphuric acid. An oily layer formed on the surface. This was removed with a separating funnel and boiled for twenty-four hours with two portions of distilled water in a flask fitted with a long tube. By this means the soluble acids are separated from the insoluble. Each twelve hour extraction was distilled separately with steam, and the distillate treated with normal hydrochloric acid. For the first portion 0.4 cc. of the acid was required, and 0.6 cc. for the second portion. The final result was 0.1151 gm. as the weight of the soluble fatty acids.

The insoluble portion of the acids was dissolved with ether. The ether was removed by evaporation, and the residue was placed in a freezing mixture. The acids crystallised in white needles at -11°. Three tests were made of the melting-point, which was round to be 9°, 11°, and 13°. The results point to oleic acid.

Two centimetres of the oils as originally extracted were found to weigh 1.7595 grms., which would make the specific gravity 0.8797.

I wish to express my thanks to Dr. N. Knight for advice and assistance in this work.

Cornell College, Mount Vernon, Iowa,
March 26, 1909.

ON THE PREPARATION AND THE COMPOSITION OF THE ACID CARBONATES OF CALCIUM AND BARIUM.

By EDWARD H. KEISER and SHERMAN LEAVITT.

THE acid carbonates of calcium, strontium, and barium have never been isolated or separated from solution as far as we have been able to find by searching the chemical literature at our command. We first attempted to isolate these acid carbonates by adding an excess of alcohol and ether to the aqueous solution of the acid carbonate, made by conducting an excess of carbon dioxide through the hydroxide. A white flocculent precipitate was formed but it rapidly decomposed, giving off carbon dioxide. Several experiments made in this way convinced us that at the ordinary temperature of about 15°, the acid carbonate of calcium decomposes rapidly into the normal carbonate and carbon dioxide and water, and that in order to isolate this compound the temperature must not be allowed to rise much above zero.

We now attempted to prepare the acid carbonate of calcium by precipitating a solution of calcium chloride with a solution of bicarbonate of potassium, keeping the temperature in the neighbourhood of zero. 5.5 grms. of pure calcium chloride were dissolved in 50 cubic centimetres of water in one beaker, and 20 grms. of bicarbonate of potassium were dissolved in 50 cc. of water in another beaker; both solutions were cooled to 0° C. by placing each beaker into a freezing mixture of ice and salt. Thereupon the bicarbonate of potassium solution was poured into the calcium chloride solution. Instantly a heavy white flocculent precipitate was formed. This was rapidly filtered by suction upon a hardened filter, and the precipitate washed with alcohol and ether and dried between folds of filtering-paper. A little of the precipitate was added to water containing a drop of phenolphthalein. The indicator remained colourless. Upon warming, however, bubbles of gas were given off, and in a few moments the solution became pink. Some of a similar solution was allowed to stand and acquire the temperature of the air; in the course of an hour and a-half it also became pink. The bubbles of gas could be seen coming off from the precipitate quite rapidly until finally the crystalline normal carbonate was left.

The experiment was repeated. This time the filtering funnel had a copper jacket around it with a space of about an inch between the funnel and the jacket. This space was kept packed with ice and salt. The precipitate was washed with absolute alcohol and ether; the latter had stood over calcium chloride for twelve hours and had then been distilled over metallic sodium to make it anhydrous.

The filter-paper on which the precipitate was finally dried was kept in a deep glass trough which had been placed in a large clay sink. The space between the trough and the sink was kept packed with ice and salt. The alcohol and ether that were used in washing the precipitate were also kept in ice and salt until used.

The dried acid calcium carbonate in the form of a fine

powder was poured into a weighing tube, tightly stoppered, and weighed. In the course of two or three minutes, as the temperature of the weighing tube rose, the dry compound became pasty, and considerable gas was given off, sufficient to eject the stopper out of the tube with force. The open tube was then heated in an air-bath to 120° to constant weight and the loss in weight determined.

Weight of acid carbonate taken..	0.4900	0.5716
Loss on drying at 120°	0.2663	0.2906
Per cent	53.7	50.8

The dry residue that was left was examined in each case, and was found to contain some potassium chloride, so that evidently the precipitate had not been washed sufficiently.

In the next series of experiments, ammonium bicarbonate was used as the precipitating agent instead of potassium bicarbonate, as it was thought that the ammonium chloride could be more readily washed out of the precipitate. 5.3 grms. of calcium chloride were dissolved in 50 cc. of water, and 15 grms. of ammonium bicarbonate in 100 cc. of water, and both solutions kept at zero by means of ice. The bicarbonate was then poured into the calcium chloride solution. The precipitate was filtered upon paper in an ice-jacketed funnel, and was washed first with ice-cold water saturated with carbon dioxide, then with ice-cold alcohol, and finally with ice-cold ether. The precipitate was then dried as before by pressing between filter-paper in the trough surrounded by the freezing mixture. The whole operation was carried on in the storage room of an ice plant where the air temperature was near zero. Weighed quantities of the acid calcium carbonate were dried in an air-bath at 120° and the loss determined. The results were—37.1, 51.19, and 51.68 per cent.

The residue obtained in each of these three separate preparations was examined quantitatively, and gave 56.3 per cent CaO in the first and 56.03 and 56.0 in the second and third residues, thus showing that pure calcium carbonate was left in each case. The first sample of acid calcium carbonate had evidently undergone partial decomposition.

From these results it is evident that the acid carbonate of calcium can be formed by double decomposition, and that it can be separated from the solution and analysed provided the temperature is not allowed to go more than one or two degrees above zero. Even at this temperature there is slow decomposition as shown by the variation in the analytical results. Our results also indicate that the composition of the acid calcium carbonate is different from that ordinarily assumed for it. This compound by analogy with the acid carbonates of the alkali metals is written $\text{H}_2\text{Ca}(\text{CO}_3)_2$; our results agree more closely with the formula $\text{Ca}(\text{CO}_3)_{1.175}(\text{H}_2\text{CO}_3)$.

The acid carbonate of barium was prepared by dissolving 12 grms. of crystallised barium chloride in 50 cc. of water and precipitating the ice-cold solution with 15 grms. of crystallised ammonium bicarbonate dissolved in 100 cc. of water and cooled to zero. The washing and filtering of the precipitate were carried out as described above. In each preparation the precipitate was washed with ice water saturated with carbon dioxide, then with alcohol and ether, and finally it was dried on the cold filter-paper in the ice trough. Five preparations were made and analysed, showing the following percentage loss of weight on drying at 120°:—(1) 16.4, 16.3; (2) 25.48, 23.01; (3) 47.18, 39.87; (4) 38.52, 37.43; (5) 40.86, 39.75.

Evidently the first and second preparations had undergone partial decomposition, and the high results in the first determination of the third preparation must have been due to the presence of a small quantity of ether which had not evaporated. The remaining analyses indicate that the acid carbonate of barium, like that of calcium, has a higher proportion of carbonic acid than is ordinarily assigned to it. Our results show that the acid carbonate of barium, like that of calcium, can be prepared by double decomposition of an alkali bicarbonate and

barium chloride, provided the temperature be kept near zero. The barium acid carbonate can be separated from the solution, washed, and dried, but owing to slow decomposition it is difficult to determine its quantitative composition.

In preparing it, it is also necessary to have the solutions not too dilute. If the solutions are diluted with ice water to three or four times the volumes mentioned, and then mixed, they remain perfectly clear because of the solubility of acid barium carbonate. Now, on heating the clear solution, as the temperature goes up, the normal carbonate is precipitated in granular form.

The experiments described in this paper were made during the winter of 1903-04.—*Journal of the American Chemical Society*, vol. xxx., p. 1711.

THE SYNTHESIS, CONSTITUTION, AND USES OF BAKELITE.*

By L. H. BAEKELAND, Sc.D.

(Continued from p. 202).

In all these processes there is a further treatment by which the solvent is driven off during a *drying* process. For example, in the process of Smith or Luft, alcohol or glycerin is thus expelled partially; and in Story's process the excess of phenol is driven off in the same way by slow drying under 100° C. In all these drying processes some of the solvent is left, either purposely so as to insure flexibility or plasticity, or it is left involuntarily, because at temperatures of 100° C. or below it is impossible to expel the totality of these solvents, part of which are stubbornly retained by the mass.

If I except the processes of Blumer, Thurlow, or DeLaire, and generally those which have in view fusible and soluble resins, in all above-mentioned patent specifications temperatures of 100° C. or much below are insisted upon.

And yet I have convinced myself by often repeated experiments that temperatures above 100° C. and considerably above 100° C. are best suited or indispensable for the complete and rapid transformation into a final insoluble, infusible product of exceptionally desirable qualities. If this be so why have my predecessors not used temperatures above 100° C.?

Why do some of them recommend temperatures as low as 80° C. (Story) and even 50° C. (Luft)? Why do they prefer to make this final hardening a long and slow operation which does not give the best, the hardest, the most resisting product? (See confirmation of my statement by Story in Belgian addition patent 210965, September 30, 1908).

For the simple reason that if their initial mass be heated at too high a temperature it gives off gaseous products, mainly composed of formaldehyde; this produces bubbles in the mass, makes it spongy, porous, and unfit for commercial use.

More direct experiments have proved to me that during the first stages of the process, we have to deal with a phenomenon that has all the characteristics of chemical dissociation with liberation of CH_2O .

If the initial mass be heated at temperatures above 100° C. the tension of this gas becomes very pronounced. At 100° C. the tension may become as high as 1 kilogram. per square centimetre (above atmospheric pressure), but this tension subsides as soon as the final product is formed.

I shall explain later how I have utilised this knowledge to good advantage, and how I counteract this dissociation simply by exercising a compensating external pressure.

In the historical part of my paper, reference has repeatedly been made to the use of condensing agents. We

* Read before the New York Section of the American Chemical Society on February 5, 1909. From the *Journal of Industrial and Engineering Chemistry*, i., No. 3.

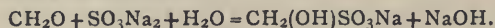
have seen how Kleeberg, Smith, Luft, Fayolle, Blumer, and Thurlow use acid condensing agents. Others, like Speyer, Hentsche, Lederer, Manasse, DeLaire, use alkalis, but every time in relatively large proportions—practically one molecule or over; but the products thus obtained are of a nature very different from the substance I am about to describe.

Story, on the other hand, adds no condensing agents whatever. True, he is able, with commercial impure carbolic acid, to obtain a reaction after about eight to ten hours' boiling, and this heating process has then to be supplemented by much longer drying. But if his process be carried out with pure or crystallised phenol, it takes many days of continuous boiling before a reaction sets in; even then the product obtained is of a dubious character, hovering between a resin of class one (fusible and soluble) and a resin of class two (infusible and insoluble). It is more likely to be a fusible and soluble resin if for some reason or another the process has been carried out with an excess of phenol, or if, some way or another, too much CH_2O has escaped in the after concentration. For instance, by following his description and boiling for five days in a return condenser a mixture of 50 grms. pure crystalline phenol and 30 grms. 40 per cent commercial formaldehyde, then concentrating in an open dish, I obtained the fusible soluble resin of Blumer or Thurlow, which on further heating remains fusible and does not change into the insoluble infusible product as described by Story. I obtain the same result if the boiling be carried on in presence of a small amount of any acid, any acid salt, or any salt which on hydrolysing may split, so as to give a preponderant acid reaction. This effect is shown by salts of mineral acids and heavy metals; it is shown even with ammonium chloride, and on acting upon formaldehyde liberates free hydrochloric acid (see Cambier, Brochet, *Comptes Rendus*, cxx., 557).

On the other hand, if I use an alkaline salt or a salt, which on hydrolysing splits into a weak acid and a strong base, as, for instance, sodium acetate, I obtain under the same circumstances a resin of the insoluble, infusible variety, even if to some extent a slight excess of phenol has been used, showing conclusively that within certain limits the amount of phenol does not change the general character of the reaction. All that may happen in that case is that the final product is rendered impure by some excess of phenol which can be driven off afterwards by a drying process similar to that of Story.

I have obtained similar results with many other alkaline salts, as, for instance, ammonium carbonate, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, trisodium phosphate, borax, potassium cyanide, sodium silicate, soap, &c.

In the same way I have used sodium sulphite, which on acting on CH_2O liberates sodium hydroxide according to following reaction:—



I might say that a similar effect is obtained from all substances which can act directly or indirectly as bases.

In other terms: *the quality as well as the quantity of condensing agent has an enormous influence on the nature of the final products.*

For the manufacture of insoluble, infusible condensation products of formaldehyde and phenol, bases used in moderate amounts have very decided advantages. They accelerate the reaction without degenerating same into a violent and irregular process. The relatively small amount of base which may remain present in the finished product, either in combined or uncombined form, does not involve the same objectionable features for its technical uses as the presence of free acid.

Furthermore, for some reason or another acid condensing agents seem to favour the formation of soluble and fusible resins, while for some other reason, bases seem to favour the formation of insoluble, infusible resins.

Moreover, by the use of small amounts of bases, I have

succeeded in preparing a *solid* initial condensation product, the properties of which simplify enormously all moulding operations as we shall see later.

I have tried all organic or inorganic bases which I could obtain readily. I have tried the hydroxides and carbonates of the alkali metals, the hydrates of alkaline earths, ammonia and its alkaline salts, hydroxylamine, organic amines, pyridine, carbamide, and other amides of weak acids; and the effect, with slight variations, is always about the same; it is quite natural, that for reasons of economy or expediency, I should prefer the commercially more available bases.

I wish it distinctly understood that in order to obtain my technical effect I use the bases in relatively small quantities, say less than one-fifth of the amount which would be required to transform the phenol into phenolate.

If larger amounts of base be used, the results are technically much inferior; in fact the process changes gradually into such as give phenol-alcohols or compound condensation products of ammonia or amines with formaldehyde, all products very different from those I desire to make.

I have good reason to believe that in my process the bases only act as catalysers and intervene only temporarily in the reaction. They seem to be expelled in free condition during the last stage of the process. For instance, if I use ammonia I find this ammonia back in the free state in the final hard condensation product.

A careful study of the condensation process of phenols and formaldehyde made me discover that this reaction, instead of occurring in two stages, can be carried out in three distinct phases. This fact is much more important than it appears at first sight. Indeed it has allowed me to prepare a so-called *intermediate condensation product*, the properties of which simplify still further my methods of moulding, and enlarge very much the scope of useful applications of my process.

The three phases of reaction can be described as follows:—

First Phase.—The formation of a so-called *initial condensation product*, which I designate as A.

Second Phase.—The formation of a so-called *intermediate condensation product*, which I designate as B.

Third Phase.—The formation of a *final condensation product*, which I designate as C.

As to the properties of each of these condensation products I can define them in a few words:—

A, at ordinary temperatures, may be liquid, or viscous, or pasty, or solid. Is soluble in alcohol, acetone, phenol, glycerin, and similar solvents; is soluble in NaOH. *Solid A* is very brittle and melts if heated. All varieties of A heated long enough under suitable conditions will change first into B, then finally into C.

B is solid at all temperatures. Brittle but slightly harder than solid A at ordinary temperatures; insoluble in all solvents, but may swell in acetone, phenol, or terpeneol without entering into complete solution. If heated does not melt, but softens decidedly and becomes elastic and somewhat rubber-like, but on cooling becomes again hard and brittle. Further heating under suitable conditions changes it into C. Although B is infusible it can be moulded under pressure in a hot mould to a homogeneous, coherent mass, and the latter can be further changed into C by the proper application of heat.

C is infusible, insoluble in all solvents; unattacked by acetone, indifferent to ordinary acids, or alkaline solutions; is destroyed by boiling concentrated sulphuric acid, but stands boiling with diluted sulphuric acid; does not soften to any serious extent if heated, stands temperatures of 300° C.; at much higher temperatures begins to be destroyed and chars without entering into fusion. It is a bad conductor of heat and electricity.

The preparation of these condensation products A and B and their ultimate transformation into C for technical purposes constitute the so-called Bakelite process. This can be described easily:—

I take about equal amounts of phenol and formaldehyde and I add a small amount of an alkaline condensing agent to it. If necessary I heat. The mixture separates in two layers, a supernatant aqueous solution and a lower liquid which is the initial condensation product. I obtain thus at will either a thin liquid called *Thin A* or a more viscous mass, *Viscous A* or a *Pasty A*, or even if the reaction be carried far enough, a *Solid A*.

Either one of these four substances are my starting materials, and I will show you now how they can be used for my purposes.

If I pour some of this *A* into a receptacle and simply heat it above 100°C ., without any precaution, I obtain a porous spongy mass of *C*. But bearing in mind what I said previously about dissociation, I learned to avoid this, simply by opposing an external pressure so as to counteract the tension of dissociation. With this purpose in view, I carry out my heating under suitably raised pressure, and the result is totally different.

This may be accomplished in several ways, but is done ordinarily in an apparatus called a Bakeliser. Such an apparatus consists mainly of an interior chamber in which air can be pumped so as to bring its pressure to 50 or better 100 lbs. per square inch. This chamber can be heated externally or internally by means of a steam jacket or steam coils to temperatures as high as 160°C . or considerably higher, so that the heated object during the process of Bakelising may remain steady under suitable pressure which will avoid porosity or blistering of the mass.

For instance, if I pour liquid *A* into a test-tube, and if I heat in a Bakeliser at say 160 – 180°C ., the liquid will change rapidly into a solid mass of *C* that will take exactly the shape of its container; under special conditions it may affect the form of a transparent hard stick of Bakelite. It is perfectly insoluble, infusible, and unaffected by almost all chemicals, an excellent insulator for heat and electricity, and has a specific gravity of about 1.25.

It is very hard, cannot be scratched with the finger nail; in this respect it is far superior to shellac and even to hard rubber. It misses one great quality of hard rubber and celluloid, it is not so elastic nor flexible. Lack of flexibility is the most serious drawback of Bakelite. As an insulator, and for any purposes where it has to resist heat, friction, dampness, steam, or chemicals it is far superior to hard rubber, casein, celluloid, shellac, and in fact all plastics. In price also it can splendidly compete with all these.

Instead of pouring liquid *A* into a glass tube or mould I may simply dip an object into it or coat it by means of a brush. If I take a piece of wood, and afterwards put it into a Bakeliser for an hour or so, I am able to provide it rapidly with a hard brilliant coat of Bakelite, superior to any varnish and even better than the most expensive Japanese lacquer. A piece of wood thus treated can be boiled in water for hours without impairing its gloss in the slightest way. I can dip it in alcohol or other solvents, or in chemical solutions, and yet not mar the beautiful brilliant finish of its surface. But I can do better, I may prepare an *A*, much more liquid than this one, and which has great penetrating power, and I may soak cheap, porous soft wood in it, until the fibres have absorbed as much liquid as possible, then transfer the impregnated wood to the Bakeliser and let the synthesis take place in and around the fibres of the wood. The result is a very hard wood, as hard as mahogany or ebony, of which the tensile, and more specially the crushing strength, has been considerably increased and which can stand dilute acids or water or steam; henceforth it is proof against dry rot. I might go further and spend a full evening on this subject alone, and tell you how we are now bringing about some unexpected possibilities in the manufacture of furniture and the wood-working industry in general. But I intend to devote a special evening to this subject and show you then how with cheap soft wood we are able to accomplish results which never have been obtained even with the most expensive hard wood.

In the same way I have succeeded in impregnating cheap ordinary cardboard or pulp-board and changing it into a hard resisting polished material that can be carved, turned, and brought into many shapes. I might take up much more of your time by simply enumerating to you the applications of this impregnation method with wood, paper, pulp, asbestos, and other fibrous and cellular materials; how it can be applied for fastening the bristles of shaving brushes, paint brushes, tooth brushes; how it can be used to coat metallic surfaces with a hard resisting protecting material; how it may ultimately supplant tin in canning processes; but I have no doubt that your imagination will easily supply you a list of possible technical uses even if I defer this subject for some other occasion.

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, March 25th, 1909.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

GEORGE Ellery Hale, Hugo Kronecker, Emile Picard, and Santiago Ramón y Cajal were elected Foreign Members of the Society.

Papers were read as follows, the summaries here printed having been supplied by the authors for use at the meeting:—

"Liberation of Helium from Radio-active Minerals by Grinding." By J. A. GRAY, B.Sc. (Melbourne).

1. Helium is liberated from thorinite, and a liberation of 28 per cent has been effected.
2. The smaller the mineral is ground the more helium is liberated.
3. This liberation has a temporary limit when the mineral is reduced to a size of about 3μ .
4. It is impossible to say how the remaining 72 per cent of helium is contained in the mineral, and to how much finer than 1μ the mineral would have to be reduced to liberate the helium.

"The Expulsion of Radio-active Matter in the Radium Transformations." By SIDNEY RUSS, B.Sc., and WALTER MAKOWER, B.A., B.Sc.

When the radium emanation is transformed into radium *A* the process is accompanied by the emission of α -particles with a velocity of 1.70×10^9 centimetres per second. The portion of the atom from which the α -particle has been emitted, which constitutes the radium *A*, must therefore recoil in a direction opposite to that in which the α -particle is projected. If we further consider that the mass of the α -particle is 4 ($H = 1$), and that of the active deposit of the order 100, it follows that at the moment of its formation this product must be travelling with a velocity of the order 10^7 centimetres per second.

In ordinary circumstances, when the emanation is mixed with air at atmospheric pressure, the radium *A* particle will possess only sufficient energy to permit it to travel a fraction of a millimetre before being stopped by collision with air molecules. On the other hand, at very low pressures, these particles should travel considerable distances without being stopped by the rarefied air, and come to rest on the enclosure containing the emanation. The case is similar for the formation of radium *B* from radium *A*.

To investigate these phenomena, discs were suspended, *in vacuo*, above surfaces rendered active by the various disintegration products of radium, and the activity obtained on the discs after exposure was measured in the normal manner by a quadrant electrometer.

The principal results obtained in this paper may be summarised as follows:—

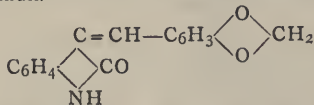
1. When radium emanation, in radio-active equilibrium with its products of disintegration, is condensed at the bottom of an evacuated tube immersed in liquid air, active deposit-particles are radiated up the tube. This phenomenon is ascribed to the recoil of the residual atom when an α -particle is emitted.
2. The law of absorption of this radiation both in air and hydrogen has been investigated. The radiation reaching a surface at a fixed distance from the condensed emanation is an exponential function of the gas pressure.
3. From the rate of decay of the activity collected on a surface exposed to the radiation from the emanation it appears that both radium A and radium B reach the surface.
4. Radium B and radium C are both radiated through a vacuum from a surface previously rendered active by exposure to the emanation. Supposing that radium B emits only β -particles, the radiation of radium C must be due to the recoil of the atoms when β -particles are emitted.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlviii., No. 11, March 15, 1909.

New Isomer of Indigo.—A. Wahl and P. Bayard.—Oxindol condenses with aromatic aldehydes, giving crystalline coloured compounds. The product with piperonal has the formula—



This reaction appears to be very general, and the author suggests the name isoindogenides for the products, which are isomeric with the indogenides formed from indoxyl. Oxindol also condenses with isatin, and thus a new isomer of indigotin is produced. This isomer is 3.3-bis-indol-indigo, and is the second chemical isomer of indigotin, the existence of which has been foretold from theoretical considerations.

Condensation of Mesoxalic Ethers with Phenol Ethers.—A. Guyot and G. Estéva.—Sulphuric acid causes the condensation of mesoxalic ethers with anisol, phenetol, &c. The reaction takes place in two phases; first, a substituted phenyltartronic ether is formed,

$\text{RO.C}_6\text{H}_4-\text{C} \begin{array}{c} \diagup \quad \diagdown \\ \text{CO}_2\text{R} \quad \text{OH} \\ \diagdown \quad \diagup \\ \text{CO}_2\text{R} \end{array}$, and then a substituted diphenyl-malonic ether, $\text{RO.C}_6\text{H}_4 > \text{C} \begin{array}{c} \diagup \quad \diagdown \\ \text{CO}_2\text{R} \quad \text{CO}_2\text{R} \end{array}$. Generally a mixture of two compounds is obtained, and is easily split into its constituents by crystallisation or fractional distillation under reduced pressure.

Action of Caustic Potash on Borneol, Camphor, and Isoborneol. Racemic Campholic Acid.—Marcel Guerbet.—*d*- and *l*-borneol when heated with anhydrous caustic potash are transformed into the corresponding campholic acids according to the equation $\text{C}_{10}\text{H}_{18}\text{O} + \text{KOH} = \text{C}_{10}\text{H}_{17}\text{KO}_2 + \text{H}_2$. In addition camphor is formed. Under the same conditions isoborneol is transformed into inactive campholic acid, which is identical with the racemic acid obtained from a mixture of equal parts of the *d*- and *l*-acids. It possesses physical properties different from those of its active isomers.

Berichte der Deutschen Chemischen Gesellschaft.

Vol. xlii., No. 4, March 6, 1909.

Colour of Fluorescence and Solvent.—Hans Stobbe.—The author has systematically studied the fluorescence of 1-phenyl-naphthalene-2.3-dicarboxylic acid anhydride in different solvents. He finds that the substance does not fluoresce in certain groups of compounds, the alkyl iodides, ethers, and acid esters. The fluorescence in bromine and chlorine compounds is strongest, and the colour is more inclined to be dark blue or violet in compounds rich in halogen. The fluorescence is violet in almost all solvents containing chlorine. These facts seem to point to the formation of a molecular complex as a cause of the colour of the fluorescence. The phenomenon is also dependent upon the physical properties of the solvent.

MEETINGS FOR THE WEEK.

FRIDAY, 30th.—Society of Dyers and Colourists, 8. Annual Meeting. "Recent Developments of the Theory of the Colloidal State, and their bearing on the Dyeing and Cleaning of Textile Fibres," by E. Feilman.

MONDAY, May 3rd.—Royal Society of Arts, 8. (Cantor Lectures). "Aerial Flight," by F. W. Lanchester.
— Royal Institution, 5. General Monthly Meeting. Society of Chemical Industry, 8. "Vulcanisation Tests in Plantation Rubbers," by C. Beadle and H. P. Stevens. "The Indian Magnesite Industry," by H. H. Dains. "New Steam Meter," by A. Girdler. "New Refractometer," by J. Lewkowitsch.

TUESDAY, 4th.—Royal Institution, 3. "Cosmogonical Questions," by Prof. Svante Arrhenius, D.Sc.

WEDNESDAY, 5th.—Royal Society of Arts, 8. "English Furniture Design and Construction," by P. A. Wells.
— Society of Public Analysts, 8. "Analysis of Air," by W. J. A. Butterfield. "Estimation of Iron by Permanganate in presence of Hydrochloric Acid," by G. C. Jones and J. H. Jeffery. "The Composition of Butter from a Cheshire Herd of Cows," by A. Smetham. "Rapid Method for the Estimation and Separation of Milk-sugar and Cane-sugar in Sweetened Condensed Milk," by I. S. Jamieson.

THURSDAY, 6th.—Royal Institution, 3. "Aspects of Applied Aesthetics," by James Paterson, A.R.S.A.
— Chemical, 8.30. "Affinity Constants of Hydroxyl- and Alkoxyl Acids," by A. Findlay, W. E. S. Turner, and Miss G. E. Owen. "Absorption Spectra of the Nitrates in relation to the Ionic Theory," by E. C. C. Baly, Miss K. A. Burke, and Miss E. G. Marsden. "Chlorination of Acetanilide," by W. J. Jones and K. J. P. Orton. "Esterification Constants of Substituted Acrylic Acids—Part IV," by J. J. Sudborough and M. J. P. Davies. "Action of the Halogens upon Aromatic Hydrazines," by F. D. Chattaway. "Studies in the Camphane Series—Part XXVI. Aryl Derivatives of Iminocamphor," by M. O. Forster and T. Thornley. "Retarding Effect of Oxygen on the Rate of Interaction of Chlorine and Hydrogen," by D. L. Chapman and P. S. MacMahon. "Colour of Aqueous Solutions of Violuric Acid," by F. G. Donnan and W. Schneider. "Molecular Volumes and Solution Volumes of Colloidal Carbohydrates," by C. F. Cross and E. J. Bevan. "Examination of Irritant Satinwood," by S. J. M. Auld. "Substituted Dihydrobenzenes—Part III. The So-called 1.1-Dimethyl- Δ^2 :5-cyclohexadiene of Harries and Antoni," by A. W. Crossley and Miss N. Renouf. "Diazo-hydroxyl-amine Compounds and the Influence of Substituting Groups on the Stability of their Molecules," by N. L. Gebhard and H. B. Thompson.

FRIDAY, 7th.—Royal Institution, 9. "The Campaign against Malaria," by Major Ronald Ross, F.R.S.

SATURDAY, 8th.—Royal Institution, 3. "Edmund Burke," by Prof. Walter Raleigh, M.A.

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DIAMONDS.

A Lecture delivered before the British Association at Kimberley.

By SIR WILLIAM CROOKES,
Hon. D.Sc. (Oxford, Dublin, and Cape of Good Hope), F.R.S.

16, NEWCASTLE ST., FARRINGTON ST., E.C.

THE CHEMICAL NEWS.

VOL XCIX., No. 2580.

ON THE QUANTITATIVE ESTIMATION OF TELLURIUM.

By A. GUTBIER and F. FLURY.

In a communication which we have only recently noticed, published in this journal, E. McIvor (CHEMICAL NEWS, 1903, lxxxvii., 17 and 163) has reported that he has obtained thoroughly satisfactory results in the estimation of tellurium by the application of G. Frerichs's gravimetric method (*Journ. Prakt. Chem.*, 1902, [2], lxxvi., 261).

As his conclusions are not in accordance with ours, we are compelled in this place once more to draw attention to the work published in the year 1905 by A. Gutbier and W. Wagenknecht (*Journ. Prakt. Chem.*, 1905, [2], lxxi., 54), and to record four new analyses that we have carried out.

As is well known the process of G. Frerichs consists in treating tellurium dioxide in presence of hydrochloric or sulphuric acid with potassium iodide and sulphurous acid, and weighing the resulting precipitate.

A. Gutbier and W. Wagenknecht obtained by most careful observation of the conditions laid down by G. Frerichs, and with an extremely pure tellurium dioxide, the results given in Table I.

TABLE I.

TeO ₃ used.	Te found.	Te found.
Grm.	Grm.	Per cent.
0.2029	0.1791	88.20
0.2198	0.1843	83.80
0.2708	0.2249	83.00
0.2316	0.1918	82.80
0.2873	0.2472	86.04
0.3138	0.2648	84.40
0.2528	0.2145	84.80
0.2787	0.2337	83.80
0.1599	0.1334	83.42
0.3026	0.2590	85.60
0.4121	0.3679	89.28
0.2631	0.2289	87.00

(Calculated percentage of Te = 79.95).

From this table it is to be seen that the results by the G. Frerichs method do not all agree with one another or with the theoretical amount.

As the tellurium dioxide was very pure, and gave by other methods excellent results, the precipitates of tellurium were thoroughly examined.

They all proved to be free from tellurium dioxide and from potassium, but, however, contained iodine which could not be removed even by continued and systematic washing for some hours.

Hence the tellurium precipitates obtained in this way always contain tellurium tetraiodide in varying proportions depending on the amount of potassium iodide used. The great affinity of iodine for tellurium which A. Gutbier and F. Flury have extensively reported is therefore in this case very conspicuous (*Zeit. Anorg. Chem.*, 1902, xxxii., 108).

G. Frerichs himself has reported to one of us that a new investigation carried out by him fully bears out the results of A. Gutbier and W. Wagenknecht.

Nevertheless, after the appearance of McIvor's publication, we have once more repeated our previous estimations, and working quite exactly according to G. Frerichs's data have obtained the results shown in Table II.

As the tellurium dioxide which we used for these analyses was derived from a sample used for atomic weight determination of tellurium, and as all the precipitates of tellurium once more contained iodine, the former results

of A. Gutbier and W. Wagenknecht are thoroughly supported.

TABLE II.

TeO ₂ used.	Te found.	Te found.
Grm.	Grm.	Per cent.
0.1003	0.0843	84.04
0.2076	0.1843	88.77
0.1870	0.1626	86.41
0.1086	0.0922	84.89

(Calculated percentage of Te = 79.95).

The formation of tellurium tetraiodide cannot be prevented by any means, and therefore it is absolutely impossible to carry out the quantitative estimation of tellurium by G. Frerichs's method.

Erlangen, Chem. Lab. of the University, and
Würzburg, March, 1909.

THE YORK AIR TESTER

FOR THE RAPID ESTIMATION OF CARBON DIOXIDE IN AIR.

THE danger associated with the presence of a large proportion of carbon dioxide in air has long been recognised by scientifically trained minds, but up to the present day the strictly physiological limit has never been actively enforced. While factory and other regulations have led to the apportioning of so many cubic feet of air space to an employee in a workshop, or to a child in a classroom, the method is, after all, only an unscientific attempt to regulate the volume of pure air to the number of individuals using the room. The details as to cubic capacity per worker are clearly defined, but the purity or impurity of the air which is being breathed is left almost unconsidered in existing Acts. Of late years the principle of "change of air per worker" as compared with "air space per worker" has been more and more recognised, and one of the factors which has somewhat delayed improvements has been the absence of a quick, but at the same time simple and accurate, method for estimating the carbon dioxide present in the air from any part of a room.

The present apparatus satisfies the three essential conditions of rapidity, simplicity, and accuracy.

The "York" Air Tester consists essentially of—(1) A wash bottle containing a definite quantity of a reagent which reacts with carbon dioxide; (2) a pump, by means of which a measured volume of air is passed through the reagent in the wash bottle.

After each stroke of the pump, the wash bottle is shaken to mix the air with the reagent, and the neutralisation point is readily seen by the sudden change of colour which the reagent undergoes. From the volume of air required to produce this coloration, the number of parts of CO₂ per 10,000 of air is directly obtained by reference to the table below.

Method of Manipulation.

Before making the solution required for the test the protection tubes marked A and F in the illustration must be filled with soda-lime. These tubes serve to prevent the access of atmospheric CO₂ to the solution. This is done in the following manner:—

A small plug of cotton-wool is placed in the constricted end of each tube, followed by a layer of soda-lime, the granules of which are about the size of split peas, after which another plug of cotton-wool is inserted. The cork and tube supplied are then fixed in position.

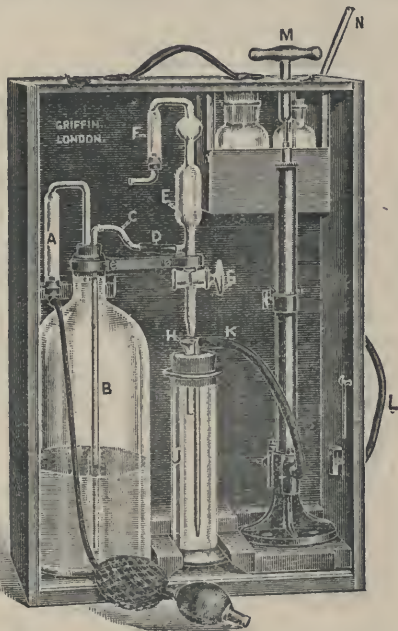
The solutions required are—(a) A strong or stock solution of baryta, from which is made (b) a weak solution which is used for the test.

Take 25 grms. of the pure crystallised barium hydroxide (powdered) and place in a 1 litre bottle; add 1 litre of distilled water, cork up, and shake well until the crystalline baryta is completely dissolved, or only the merest trace of barium carbonate left in suspension. It is very important that the rubber stopper should fit tightly so that no air can gain access to the solution. This bottle contains the

laboratory stock solution, and need not be carried about with the apparatus. An improved method of storing this solution is described below.

To prepare the weak solution, first remove the fittings from the bottle marked B, and then place in it 2 litres of distilled water and about 1 cc. of a solution of phenolphthalein (containing 1 gm. of phenolphthalein per 100 cc. of alcohol).

By means of the 5 cc. graduated pipette small quantities of the strong baryta solution are run into the 2 litres of water in the bottle B until, after thorough shaking, the solution just assumes a permanent pink tint; the CO₂ which was originally present in the distilled water has now



precipitated. As soon as this pink tint is permanent add a further 3.3 cc. of the strong baryta solution, insert a cork, and shake thoroughly. Then remove the cork, and immediately fit the rubber stopper, protecting tubes, and pipette (A, C, E, F) in position.

This solution now requires calibrating against atmospheric air. The apparatus is placed in front of an open window on the windward side of the room, in such a position that a current of fresh air is passing over it. The outlet tube of the pump is now connected to the absorption vessel J (by means of a rubber tube K), and the inlet valve to a long glass tube N (by means of a rubber tube L); the open end of N projecting several feet out of the window and being supported by passing through a ring supplied ready for attachment to the body of the pump. In this way a sample of pure air can be procured. The pump is worked several times up and down so as to clear the apparatus of any impure air.

Twenty-five cc. of the solution in the bottle B—conveniently raised into the pipette by means of the small blower attached at A—are placed in the absorption vessel J, and a drop or two of phenolphthalein solution added, through the tube H. The bottle J and its contents are then thoroughly shaken (the tube H being closed by the thumb) for a quarter of a minute, after which one volume of air from the pump is discharged into the absorption vessel J, which is again thoroughly shaken for the same length of time. During the shakings it is an advantage to place a spring clip on the rubber tube near the absorption vessel so as to prevent any of the liquid from running down the tube and into the pump valves. This process is repeated

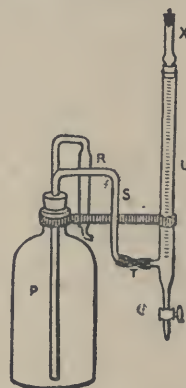
until the solution just becomes colourless, which should occur after 14 strokes of the pump, plus one added for the air present in the vessel at the commencement—15 in all. As the accompanying table has been drawn up on a basis of 15 strokes for pure air, it is necessary to adjust the strength of the solution until it responds to 15 strokes with pure air. If the solution is either too weak or too strong it is best to start again with another 2 litres of water in the bottle. With a little practice it becomes easy to hit off the correct amount of strong solution required.

Having adjusted the solution to the required strength, the apparatus can be used to test the amount of CO₂ in the air of any room. The inlet tube should be placed at some distance from the operator, at least 3 ft. from any person in the room and 3 ft. away from any wall. In an ordinary test of a workroom, the sample should be taken at about the breathing level. A reference to the following table will give directly the parts of CO₂ per 10,000 present from the number of strokes.

Strokes of pump.	Parts CO ₂ per 10,000.	Strokes of pump.	Parts CO ₂ per 10,000.
15	3.6	7½	8.7
14	4.0	7	9.3
13	4.5	6½	10.1
12	5.0	6	10.9
11	5.6	5½	11.7
10½	5.9	5	12.7
10	6.3	4½	13.8
9½	6.7	4	15.0
9	7.2	3½	16.4
8½	7.7	3	18.0
8	8.2	2½	19.8

A note of the general condition and temperature of the atmosphere, of the air space available, the number of people present, the presence or absence of gas jets, and of open windows should accompany the result of this test.

An improved method of storing the strong stock solution of barium hydroxide is shown in the illustration below. The rubber stopper closing the neck of the bottle carries inlet and outlet tubes; one, R, is trapped with soda-lime



(just as A above), while the other, S, is connected by means of the ball valve, T, with the burette U. This burette is closed at the top by a soda-lime tube X, and at the bottom by a tap.

The burette is filled from the stock-bottle P, by attaching the hand bellows to R and gently blowing, releasing the ball valve at the same time until sufficient solution has passed into U. This burette may now be used for delivering the strong solution instead of making use of the 5 cc. pipette.

In testing exceptionally foul air, it will be found that a solution of twice the usual strength gives results almost exactly corresponding with twice the CO₂ content quoted in the above table.

The apparatus is manufactured only by John J. Griffin and Sons, Ltd.

ON THE COMPOSITION OF THE ACID
CARBONATES OF CALCIUM AND BARIUM.

By EDWARD H. KEISER and LEROY McMASTER.

THE work of Keiser and Leavitt, in a preceding paper (*Journ. Am. Chem. Soc.*, xxx.; *CHEM. NEWS*, xcix., 212), has shown that it is possible to prepare the acid carbonates of calcium and barium by double decomposition and to separate them from the solution in which they have been formed. It is difficult, however, to get them in dry condition for analysis without having them undergo partial decomposition. Thinking that there may perhaps have been a trace of moisture or of ether in the compounds that were analysed, we determined to modify the method of analysis, and without attempting to dry and weigh them, to determine, for example, the ratio of barium oxide to carbon dioxide in the acid carbonate of barium.

The method of preparation was similar to that described by Keiser and Leavitt, except that we formed the compound in a solution containing gelatin. The object of the gelatin was to retard the decomposition of the acid carbonate. In order to make a series of precipitations, we made up a solution of crystallised barium chloride containing 21 grms. to the litre, one of ammonium bicarbonate, containing 31.6 grms. to the litre, and a solution of gelatin, made by boiling pure gelatin with water and diluting it to such an extent that it did not gelatinise when it was cooled to zero. This gelatin solution was neutral to phenolphthalein, litmus, and methyl-orange. The barium chloride had been re-crystallised, and the ammonium bicarbonate gave on analysis 55.2 per cent carbon dioxide instead of the theoretical 55.5 per cent. 100 cc. of the barium chloride and of the bicarbonate solutions were measured into separate beakers, and 25 cc. of gelatin solution added to each. A lump of ice was put into each, and when the temperature had fallen to zero the solutions were mixed. Precipitation did not take place immediately as when no gelatin is present, but in from five to seven minutes the acid carbonate came down. Washed carbon dioxide from a Kipp's apparatus was now passed into the beaker for about ten minutes. The liquid was now poured upon a filter and the precipitate washed five times with ice water charged with carbon dioxide. After washing, the filter with acid carbonate on it was placed in a flask and tightly stoppered with a rubber stopper, carrying a separating funnel in one hole, and in the other hole a delivery tube sealed at the end but with a hole in the side half an inch above the sealed end. This tube had been drawn up into the stopper so that when the stopper was forced into the flask no gas could escape. The flask was now packed in snow or ice until the determination of carbon dioxide was made. This much of the work was done out of doors in the morning of cold winter days, when the ground was covered with snow, and the temperature of the air was below freezing.

To determine the ratio of carbon dioxide to barium oxide in the precipitate, the flasks were removed to the laboratory and connected with the apparatus for the gravimetric determination of carbon dioxide. The delivery tube with sealed end was pushed down through the stopper until the hole opened into the flask and the gas could pass into the drying tubes and finally into the weighed potash bulb. Dilute hydrochloric acid was then admitted by means of the separating funnel and the acid carbonate completely decomposed and the carbon dioxide all swept into the weighed potash bulbs.

The barium chloride solution remaining in the flask was then filtered to remove the filter-paper, and made up to definite volume, and an aliquot part taken for the determination of barium. The latter was weighed as barium sulphate. Five preparations of acid barium carbonate were made in this way, and the results obtained from the analyses are given in Table I.

The ratio of molecules was calculated in the following way:—(BaO) : (CO₂)X : wt. of BaO : wt. of CO₂; substi-

tuting the figures 153 : (44)X : 0.4839 : 0.3716, X = 2.67. From our results it appears that the acid carbonate of barium contains more than two molecules of carbon dioxide for one of barium oxide. Our analyses would indicate some such formula as BaCO₃.1.5(H₂CO₃).

TABLE I.

	Weight of BaO.	Weight of CO ₂ .	Ratio of molecules of CO ₂ to 1 of BaO.
1.	0.4839	0.3716	2.67
2.	0.3156	0.2342	2.58
3.	0.3062	0.2286	2.60
4.	0.3823	0.2900	2.63
5.	0.3647	0.2522	2.41

Average 2.58

We have also determined the ratio of molecules of carbon dioxide to one molecule of lime in solutions of the acid carbonate of calcium at the ordinary temperature. We proceeded as follows:—Purified carbon dioxide was passed into clear lime water containing a drop of phenolphthalein until the pink colour disappeared and the calcium carbonate first formed had largely dissolved. This solution was now filtered. It contained acid calcium carbonate and excess of carbon dioxide. To remove the latter it was now rapidly agitated with air, using a turbine stirring arrangement, until the pink colour of the phenolphthalein just began to appear. The temperature was 16 to 18° C. We assume that this pink colour just appears at the point when all the excess of carbon dioxide is removed and the normal carbonate begins to be formed. Two volumes of 200 cc. each were now quickly measured off for analysis; in the one the lime was determined, in the other the carbon dioxide. The lime was found by evaporating the solution to dryness in a weighed platinum dish, and from the weight of calcium carbonate the weight of lime calculated. As pure marble lime had been used to make the original solution, and as the residue was dried at 120° in an air-bath, we assumed that it was calcium carbonate. The carbon dioxide was determined gravimetrically by treating the measured volume of the solution in a flask with hydrochloric acid and driving out the gas by heat and a current of pure air, and absorbing it in a weighed potash bulb. The results obtained are given in Table II.

TABLE II.

	Weight of CaO.	Weight of CaO ₂ .	Ratio of molecules of CO ₂ to 1 of CaO.
1.	0.0299	0.0580	2.46
2.	0.0552	0.1360	3.13
3.	0.0404	0.0980	3.08
4.	0.0657	0.1558	3.02
5.	0.0555	0.1288	2.95
6.	0.0694	0.1349	2.47
7.	0.0864	0.1943	2.86
8.	0.0207	0.0464	2.85

Average 2.84

These results indicate that the composition of the acid calcium carbonate, when in dilute solution at the ordinary temperature, must be represented by the formula containing more than two molecules of carbon dioxide for one of lime. Our results indicate the formula CaCO₃.1.8(H₂CO₃), and this agrees fairly well with the determinations of Keiser and Leavitt, who found the composition of the precipitated acid carbonate to correspond to the formula CaCO₃.1.75(H₂CO₃).

We also noticed that the solution of the acid carbonate of calcium which had been agitated with air until a faint pink colour had appeared, again became colourless on standing in the air, apparently because this solution absorbed carbon dioxide from the air. The reverse is true of a solution of acid barium carbonate; this when it has been agitated with air until it is very faintly pink and is allowed to stand, gradually becomes more deeply coloured. Appa-

rently the dissociation pressure of the carbon dioxide in the latter case is greater than in the former.

We have applied the same method of analysis to determine the composition of the acid carbonate of barium. The solution in this case was made by conducting carbon dioxide into a solution of barium hydroxide containing a drop of phenolphthalein until the pink colour had disappeared, and then continuing the current of gas until the barium carbonate had dissolved to a considerable extent. This solution of the acid barium carbonate was filtered and agitated with air until a very faint pink colour appeared. Two portions were then measured off for analysis, and the carbon dioxide and the barium oxide determined by the method described above. Table III. gives the results obtained:—

TABLE III.

	Weight of BaO.	Weight of CO ₂ .	Ratio of molecules of CO ₂ to 1 of BaO.
1.	0.0648	0.0338	1.82
2.	0.0514	0.0414	2.81
3.	0.1786	0.1083	2.11
4.	0.0557	0.0407	2.55
5.	0.0626	0.0448	2.49
6.	0.1042	0.0755	2.52

Average, omitting No. 1 .. 2.496

These results indicate that the composition of the acid carbonate of barium in dilute solution at 15 to 16° C. has a composition expressed by the formula $\text{BaCO}_3 \cdot 1.5(\text{H}_2\text{CO}_3)$. This confirms the results that we obtained from the analysis of the precipitated acid barium carbonate.

The experiments described in this paper were made in January and February, 1908, and it is our intention in the coming winter to apply the methods described to the determination of the composition of the acid carbonates of other metals.—*Journal of the American Chemical Society*, vol. xxx., No. 11.

THE SYNTHESIS, CONSTITUTION, AND USES OF BAKELITE.*

By L. H. BAKELAND, Sc.D.

(Concluded from p. 215).

As to Bakelite itself, you will readily understand that it makes a substance far superior to amber for pipe stems and similar articles. It is not so flexible as celluloid, but it is more durable, stands heat, does not smell, does not catch fire, and at the same time is less expensive.

It makes excellent billiard balls, of which the elasticity is very close to that of ivory; in short it can be used for similar purposes like knobs, buttons, knife handles, for which plastics are generally used. But its use for such fancy articles has not much appealed to my efforts as long as there are so many more important applications for engineering purposes.

Bakelite also acts as an excellent binder for all inert filling materials. This makes that it can be compounded with sawdust, wood pulp, asbestos, colouring materials, in fact with almost anything the use of which is warranted for special purposes. I cannot better illustrate this than by telling you that here you have before you a grindstone made of Bakelite, and on the other hand, a self-lubricating bearing which has been run dry for nine hours at 1800 revs. per minute without objectionable heating and without injuring the quickly revolving shaft.

If I mix Bakelite with fine sand or slate dust I can make a paste of it which can be applied like a dough to the inside of metallic pipes or containers, or pumps, and after Bakelising this gives an acid-proof lining very useful in chemical engineering.

Valve seats which are unaffected by steam, steam-packing that resists steam and chemicals, have been produced in a similar way.

Phonograph records have been made with it, and the fact that Bakelite is harder than rubber, shellac, or kindred substances indicates advantageous possibilities in that direction.

For the electrical industry Bakelite has already begun to do some useful work. There too its possible applications are numerous. Armatures or fields of dynamos and motors, instead of being varnished with ordinary resinous varnishes, can simply be impregnated with A, then put into a Bakeliser, and everything transformed into a solid infusible insulating mass; ultimately this may enable us to increase the overload in motors and dynamos by eliminating the possibility of the melting or softening of such insulating varnishes as have been used until now. But the subject of dynamos and motor construction is only at its very modest beginnings, and I prefer to mention to you what has been already achieved in the line of moulded insulators of which you will find here several very interesting samples.

This brings me to the subject of moulding Bakelite.

For all plastics like rubber, celluloid, resins, &c., the moulding problem is a very important one. Several substances which otherwise might be very valuable are useless now because they cannot economically be moulded. The great success of celluloid has mainly been due to the fact that it can easily be moulded. Nitrated cellulose alone is far superior in chemical qualities to celluloid, but until Hyatt's discovery, it could only be given a shape by an evaporation process, and its applications were very limited. The addition of camphor and a small amount of solvent to cellulose nitrate was a master-stroke, because it allowed quick and economic moulding.

In the same way white sand or silica would be an ideal substance for a good many purposes, could it be easily compressed or moulded into shape and into a homogeneous mass. But it cannot; and therefore remains worthless. And that is the main difference between a plastic and a non-plastic. It so happens that Bakelite in C condition does not mould; it does not weld together under pressure even if heated; only with much effort is it possible to shape some kind of an object out of it, but some way or another the particles do not stick well together; in other terms it is not a true plastic. Therefore the moulding process has to be solved in the anterior stages of the process. We have seen how Smith, Luft, and Story tried to solve a similar problem by the admixture of solvents and subsequent evaporation, but we know now that these very solvents imply most serious drawbacks.

I have already shown you how I am able to mould and harden quickly by pouring liquid A into a mould and heating it in a Bakeliser. But even that method is much too slow for most purposes. Furthermore, moulds cost money; any rubber or celluloid manufacturer will tell you that the item of moulds represents a big portion of the cost of his plant. If an order for 10,000 pieces has to be delivered, and it takes an hour for moulding, it will require between three and four years to fill this order with one mould, and if the mould cost 100 dols. it will require 5000 dols. for moulds alone if the order has to be finished within twenty days. For that very reason I have devised my moulding methods so as to use the moulds only during the very minimum of time. I have succeeded in doing so in several ways. One of the simplest ways is the following:—

As stated before, the use of bases permits me to make a variety of A that is solid although still fusible. The latter is as brittle as ordinary rosin, and can be pulverised and mixed with suitable filling materials. A mixture of the kind is introduced in a mould and put in the hydraulic press, the mould being heated at temperatures preferably about or above 160–200° C. The A melts and mixes with the filler, impregnating everything; at the same time it is rapidly transformed into B. But I have told you that B

* Read before the New York Section of the American Chemical Society on February 5, 1909. From the *Journal of Industrial and Engineering Chemistry*, i., No. 3.

does not melt, so the moulded object can be expelled out of the mould after a very short time, and the mould can again be re-filled. All the moulded articles are now in B condition; relatively brittle but infusible. At the end of the day's work or at any other convenient time all the moulded articles are put in the Bakeliser, and this of course without the use of any moulds; in this way they are finally transformed into C Bakelite of maximum strength and hardness and resisting power.

The process can still be further simplified. Instead of using A, we can use B, and mould it in the hot press, where it welds and shapes itself. After a very short time, the B begins to transform into C, and can now be expelled from the mould. If the transformation in C is not complete, a short after-treatment in the Bakeliser will finish everything. I have succeeded thus in reducing the moulding to less than two minutes for small objects.

The valuable properties of B may be used in many other ways; for instance, A may be poured into a large container, and be heated slowly at 70° C. until it sets to a rubber-like mass, and shows that it is transformed into B. This block of B if warm has very much the consistency of printers' roller-composition, but is brittle when cold. The warm flexible mass can now be removed from its container, or divided, cut, or sawed to any desired shape, and the so-shaped articles can be simply placed in a Bakeliser; no melting nor deformation can occur, so we need no mould while maximum heat is applied to bring everything in condition C.

I could multiply these examples by numerous other modifications of my process, but I believe that what I have said will be enough to convince you of its many uses; we are studying now applications of Bakelite in more than forty different industries, on some of which I shall report on some future occasion.

The chemical constitution of Bakelite and the nature of the reactions which occur in the Bakelite process are problems which I have endeavoured to solve. This subject is not by any means an easy one. Indeed, we have to deal here with a product that cannot be purified by crystallisation nor other ordinary methods, which is insoluble, does not melt nor volatilise; in other terms, it is not a product which is amenable to our usual methods of molecular weight determination. Its chemical inertness makes it unfit for studying possible chemical transformations, and unless my friends the physico-chemists will come to my aid, discover some way for establishing some optical properties or other physical constants, we are very much at a loss to establish the molecular size of my product.

But I have been so fortunate as to be able to obtain some insight into its chemical constitution by a rather roundabout way. Indeed, I have succeeded in making Bakelite by indirect synthesis.

As stated previously, oxybenzylalcohol if heated at 150° C., or in presence of acids, gives various partial anhydrides, called saliretin, which may resinify further if heated at higher temperatures. Saliretin products are more or less soluble in alcohol and acetone, and in NaOH solution, from which they may be re-precipitated by means of NaCl.

We have already seen that De Laire in heating phenol alcohols in vacuum obtains soluble resins. But I have heated saligenin in sealed tubes under pressure at 180° C. for eight hours, with and without the addition of small amounts of ammonia. In both cases I obtain a substance which is hard when cold, but which softens when heated, but does not melt. It swells in acetone and in NaOH, and dissolves partially. This substance is not my intermediate condensation product B, because no amount of heating can transform it into C.

If, however, I heat oxybenzylalcohol in presence of enough CH₂O or its polymers in a sealed tube at 180° C. for eight hours, I obtain a substance entirely similar to Bakelite in properties and in chemical composition.

By varying the proportions and repeating the experiment

a great number of times I succeeded in establishing that, unless I use at least 1 molecule of CH₂O for 6 molecules of oxybenzylalcohol, I do not obtain Bakelite but a product containing saliretin compounds.

The same result occurs by heating 6 molecules of phenol and 7 molecules of CH₂O in presence of a small amount of a base.

If I use somewhat less formaldehyde, or if for some reason or another all the formaldehyde does not enter into reaction, I obtain a substance which may still be attacked by acetone, probably because it contains uncombined phenol or saliretins after the reaction is over.

But I have found that all these substances, whether they are obtained by heating 6 molecules of phenol alcohol with at least 1 molecule of CH₂O, or whether they are obtained by the action of phenol on formaldehyde under heat and pressure in presence of small amounts of bases, can be purified and brought to about constant composition as follows:—

The substance is pulverised, washed with 5 per cent KOH solution, with dilute HCl, with alcohol, with acetone, and finally dried to constant weight *in vacuo*.

The powder so obtained still contains traces of potassium, which I did not succeed in eliminating. The amount of same is very small, about 0.09 per cent of ash, but it seems to cling tenaciously to the product, and makes it somewhat hygroscopic, making weighing for analytical purposes very difficult, and accounts for some variations in the results.

The organic combustion of all these products gave the following results:—

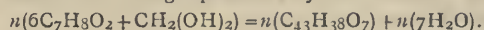
1 molecule CH ₂ O ; 6 molecules saligenin	C = 77.48 H = 5.96 O = 16.56	77.88 5.97 16.15
1 molecule CH ₂ O ; 4 molecules saligenin	C = 76.47 H = 5.44 O = 18.09	76.35 5.40 18.25
13 molecules CH ₂ O ; 12 molecules saligenin	C = 76.59 H = 5.97 O = 17.44	76.57 5.97 17.46
1 molecule phenol ; 1 molecule CH ₂ O ; and 1 per cent NH ₃ ..	C = 77.48 H = 5.60 O = 16.92	76.61 5.80 17.59
10 cc. phenol ; 10 cc. 40 per cent formaldehyde ; and 1 per cent NH ₃	C = 77.92 H = 5.71 O = 16.37	75.62 5.78 18.60 (a)

(a) Beginning oxidation during drying.

If we take into consideration the great difficulties encountered in purifying methods, these results seem to indicate that we have to deal here with a definite organic substance of constant composition, which according to its methods of preparation may exist with impurities mixed in various proportions. These impurities are probably free phenol, or free CH₂O or saliretin products.

From the indirect synthesis of Bakelite by means of oxybenzylalcohol and CH₂O, I am led to consider Bakelite in its simplest form as a polymerised oxybenzyl—methylene-glycol—anhydride which, in case of ordinary phenol, might be represented by the formula $n(C_{13}H_{18}O_7)$.

The reaction being represented by—



This formula corresponds acceptably to the analytical results if we take into consideration the difficulties of purification.

	C.	H.	O.
Calculated	77.44	5.75	16.81
Found (average) ..	77.68	5.96	16.36

(With product of 6 molecule saligenin + 1 molecule CH₂ ..

I consider Bakelite C as a direct polymer of another anhydride which is represented by my intermediate condensation product or Bakelite B. Bakelite B is a more complete anhydride than Bakelite A. As to Bakelite A, I am unable to arrive at a constant composition, for the

reason that it easily gives off water, changing gradually its composition until heating converts it slowly into B, after passing through various mixtures of A and B.

My supposition has a strong appearance of probability by the following experiment:—

If I put a mixture of phenol and formaldehyde in proper proportions and with some small amount of a base in a sealed glass tube, and heat just long enough to produce A, the formerly homogeneous liquid mixture separates into two layers. The initial condensation product A forms a lower stratum, and a supernatant layer of liquid indicates the elimination of water. The same thing occurs if anhydrous phenol is heated with paraform in presence of a small amount of base.

If this A, first properly freed from any physically retained water, be introduced into another sealed tube and heated further, I may succeed with some precaution as to the duration of heating, in stopping just in time so as to transform everything into B, the intermediate condensation product. I then see that a new amount of water is set free which will assemble on top, giving evidence of further dehydration. At the same time we notice that the mass B has not contracted in volume to any important extent.

If now this B, properly freed from water, be heated in another sealed tube, it will be transformed finally into C. But this time we see no further elimination of water. On the other hand, there is a decided contraction of volume.

This contraction of volume, together with the remarkable increase in physical and chemical inertness, points out towards the probability that C is simply the polymer of B.

I am fully supported in this belief by the fact that analysis has shown me that B and C contain the same percentage of carbon, hydrogen, and oxygen.

With homologues of phenol we obtain the direct homologues of these anhydrides; for instance, with ortho-cresol we get the polymer of ortho-methyl-oxybenzyl-methylene-glycol-anhydride.

It may be of interest to remind you that many years ago Oscar Low called our attention to the great importance of formaldehyde as a starting-point of synthesis in plant life (*Ber.*, xxii., 475; and xxiii., 388 and 480). By the photochemical action of sunlight on CO_2 in presence of water in chlorophyll, oxygen is liberated and produces CH_2O . This is the beginning of a process of further synthesis building up more complicated bodies.

If we accept these premises then the theory of the Bakelite process is easy to explain:—

Stage A.—Formation of a partial anhydride of a phenol alcohol and methylene glycol containing hydroxyl groups, which can fix NaOH .

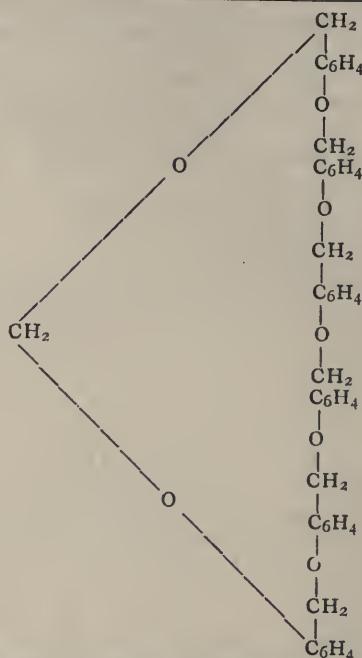
Stage B.—Formation of a higher anhydride by further elimination of water. This higher anhydride seems no longer to possess hydroxyl groups, but by addition of NaOH may still form alkaline compounds. This induces me to believe that in some way or another we shall succeed in obtaining alkali compounds of the kind which on being treated with dilute acids will regenerate A.

Until we have anything better, I shall propose the formula shown in next column.

Stage C.—Polymerisation of the B product resulting in greater chemical inertness and disappearance of active corners of the molecule.

I shall also call your attention to the fact that the willow tree produces in its cells salicin, which is the glucoside of saligenin; this same saligenin or oxybenzyl alcohol in presence of more CH_2O has given me Bakelite.

On the other hand, Bertrand (*Ann. Chim. Phys.*, 1898, [6], xii., 115; *Bull. Soc. Chim.*, 1894, [3], xi., 614 and 717), and Tschirch and Stevan (*Arch. d. Pharm.*, 1905, cclxiii., 504), and more recently R. Majima and S. Cho (*Ber.*, November, 1907, xv., 4390) have called our attention to the phenolic nature of resinous substances, specially Japanese lacquer. The latter substance has some analogy with Bakelite and exudes from the *Rhus vernicifera*, Dc., which is a plant that is somewhat related to our American poison ivy."



So after all, the synthesis accomplished in my laboratory seems to have a decided similarity to some intricate biological processes that take place in the cells of certain plants.

In order not to increase too much the length of this paper, I have merely given you the brief outlines of years of arduous but fascinating work, in which I have been ably helped by Mr. Nathaniel Thurlow, and more recently also by Dr. A. H. Gotthelf, who attended to my analytical work.

The opened field is so vast that I look forward with the pleasure of anticipation to many more years of work in the same direction.

I have preferred to forego secrecy about my work, relying solely on the strength of my patents as a protection.

It will be a great pleasure to me if, in doing so, I may stimulate further interest in this subject among my fellow-chemists, and if this may lead them to succeed in perfecting my methods or increasing still further the number of useful applications of this interesting compound.

Polychromic and Chromotropic Violurates.—A. Hantzsch and Basile Issaias.—The alkali salts of violuric acid, $\text{CO} \begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix} \begin{smallmatrix} \text{—CO} \\ \text{—CO} \end{smallmatrix} \text{C:N.OH}$, exist in at least three different coloured forms, yellow, red, and blue. One and the same alkali salt can exist in two forms, either yellow and red, or red and blue. One form is always labile as shown in the following table:—

	Yellow.	Red.	Blue.
Lithium salts ..	Labile	Stable	—
Sodium salts ..	—	Stable	Labile
K, Rb, Cs salts ..	—	Labile	Stable

Thus, as the atomic weight of the alkali metal increases, the stability of the darker coloured form also increases. The weakest alkali metal (lithium) gives the faintest coloured (yellow) form, and the strongest alkali metal (caesium) gives the strongest coloured (blue) form most readily. The apparently varying auxochromic effect of the different alkali metals is to be ascribed to the different stability of the isomeric forms. The silver salts exist only in compounds with colourless components (pyridine, silver nitrate) in colourless yellow, red, blue, and green forms.—*Berichte*, xlii., No. 5.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Annual General Meeting, March 25th, 1909.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

DR. G. BARGER and W. B. TUCK were appointed Scrutators, and the ballot was opened for the election of Officers and Council for the ensuing year.

The PRESIDENT presented the Report of the Council on the progress of the Society during the past twelve months, and the TREASURER, after making a statement as to the Society's income and expenditure for the year 1908, proposed a vote of thanks to the Auditors, which was seconded by Dr. H. G. COLMAN and acknowledged by Dr. A. HARDEN and Dr. V. H. VELEY.

The adoption of the Report of Council together with the Balance Sheet and Statements of Accounts for the year ended 31st December, 1908, was proposed by Prof. J. NORMAN COLLIE, and seconded by Mr. JOHN SPILLER. After some remarks by Dr. E. DIVERS, the motion was put to the Meeting and carried unanimously.

Report of the Council.

The Council once more have the satisfaction of stating that the prosperity of the Society continues, both the number of papers read and the number of Fellows on the list showing a considerable increase.

On December 31st, 1907, the number of Fellows was 2896. During 1908, 159 Fellows were elected, and 4 were reinstated, thus making a gross total of 3059. The Society has lost 31 Fellows by death; 38 have resigned; 2 elections have become void, and the names of 38 Fellows have been removed from the list for non-payment of Annual Subscriptions.

The total number of Fellows, therefore, at the 31st December, 1908, was 2950, showing an increase of 54 over the number for the previous year.

The names of the deceased Fellows, with the dates of their election, are:—J. H. Ball (1902), S. Banner (1888), B. H. Brough (1884), J. T. Cart (1907), A. V. Cunningham (1898), A. Deck (1874), Sir J. Evans (1876), E. A. Fasnacht (1902), R. J. Friswell (1871), Sir J. C. Gamble (1876), T. A. Gerard (1904), W. M. Habirshaw (1874), R. H. Harland (1876), F. W. Hart (1869), A. Helms (1894), A. Houldershaw (1901), R. V. Jackson (1881), J. G. Johnson (1872), W. H. Jowett (1891), F. H. Leeds (1891), T. Morson (1851), H. L. Pendlebury (1907), J. H. Player (1860), W. A. Shenstone (1876), A. Sibson (1859), F. G. Smith (1903), E. Sorstadt (1874), Sir T. Stevenson (1864), B. H. Thwaite (1880), A. Wade (1908), T. H. Walker (1879).

The following Fellows have resigned:—J. Alexander, J. A. Basker, F. W. Bayly, J. H. Belcher, L. H. Berry, W. R. Cooper, A. J. Cownley, D. C. Crichton, C. Crocker, F. W. Daw, F. A. Drake, L. Dufty, G. C. Fry, T. Gough, A. H. Green, H. L. Greville, E. G. Guest, C. G. Kiddell, W. J. Lockyer, J. Marsh, L. W. Mathieson, E. W. Millar, E. Morris, W. D. Page, H. Ross, H. Rostron, H. Senier, F. Shedden, E. C. Sherwood, E. S. Smith, W. Southworth, A. Turner, G. J. Ward, R. Waterhouse, T. Whitaker, W. H. Wood, J. W. Yates, and Professor A. Haller, whose name has been transferred from the list of Ordinary Fellows to that of the Honorary and Foreign Members.

The number of those Fellows elected prior to 1860 has been diminished by the death of Mr. Thomas Morson, elected on December 15th, 1851, and of Mr. Alfred Sibson, who was elected on December 15th, 1859.

The Council have great pleasure in congratulating Prof. William Odling and Mr. E. A. Pontifex on having reached the 60th Anniversary of their Election as Fellows of the Society; the following Fellows during the past two or

three years have reached their Jubilee as Fellows:—Prof. A. H. Church (1856), Sir W. Crookes (1857), Mr. E. Davies (1858), Mr. J. F. Davis (1857), Prof. G. Carey Foster (1856), Mr. C. Hanbury (1857), Prof. J. W. Mallet (1857), Mr. F. Norton (1854), Sir H. E. Roscoe (1855), Mr. P. J. Worsley (1858).

The number of Honorary and Foreign Members at the close of 1907 was 29. Seven were elected in February, 1908, but during the past year the Society has had to mourn the death of Prof. A. H. Becquerel and of Prof. Wolcott Gibbs, thus making the total of Honorary and Foreign Members, at the close of 1908, to be 34. Since then, however, Prof. Emil Erlenmeyer and Prof. Julius Thomsen, F.R.S., have passed away. Arrangements are being made for the preparation of Memorial Lectures, and that dealing with the life work of Prof. Wolcott Gibbs will be delivered by Dr. Frank Wigglesworth Clarke early in June.

A general scheme of co-operation with the Royal Society in the matter of Obituary Notices has been formulated; it will now be possible to issue those relating to deceased Fellows in the publications of both Societies, subject to the consent of the author.

During the year 1908, 278 scientific communications have been made to the Society, 212 of which have been published already in the *Transactions*, and abstracts of all have appeared in the *Proceedings*.

The volume of *Transactions* for 1908 contains 2281 pages, of which 2188 are occupied by 222 memoirs, the remaining 93 pages being devoted to the Obituary Notices, the Report of the Annual General Meeting, and the Presidential Address; the volume for the preceding year contains 205 memoirs, which occupy 2021 pages.

The *Journal* for 1908 contains also 4978 abstracts of papers published mainly in foreign journals, which extend to 2112 pages, whilst the abstracts for 1907 numbered 4686, and occupied 2100 pages. The abstracts for 1908 may be classified as follows:—

PART I.		Pages.	No. of Abstracts.
Organic Chemistry	1032	1879	
PART II.			
General and Physical Chemistry ..		936	
Inorganic Chemistry		588	
Mineralogical Chemistry		97	
Physiological Chemistry		567	
Chemistry of Vegetable Physiology and Agriculture		265	
Analytical Chemistry		646	
	1080	3099	
Total in Parts I. and II. ..	2112	4978	

In July, 1908, the Linnean Society celebrated the fiftieth anniversary of the presentation, by C. R. Darwin and A. R. Wallace, of the essay entitled "On the Tendency of Species to Form Varieties, and on the Perpetuation of Varieties and Species by Natural Means of Selection"; on this occasion the Chemical Society was represented by the Foreign Secretary, Dr. Horace T. Brown. Another jubilee of especial interest, held in October, was that of the Foundation of the Oxford University Museum, which followed upon the establishment of a Natural Science School at Oxford; at this ceremony the President, Sir William Ramsay, offered to the University the congratulations of the Society.

Late in 1907, the President was nominated on the deputation organised by the British Science Guild, which subsequently represented to the Postmaster-General the desirability of reducing postage rates for the publications of learned Societies; this deputation was received by the Postmaster-General on March 12th, 1908, but his reply was not sympathetic. Following this action, a memorandum on the subject was prepared, and forwarded to certain

members of Parliament, some of whom communicated in the matter with the official representatives of the Post Office in the House; the majority of these members, however, were of opinion that it is undesirable to raise this question again at present.

The Society has become indebted to Prof. J. Emerson Reynolds for a bust of Michael Faraday.

In May, 1908, a petition, signed by more than three hundred Fellows, was presented to the Council requesting them to ascertain the wishes of the Society as a whole regarding the admission of women to the Fellowship of the Society. Acceding to the request of the memorialists, the Council directed the Secretaries to issue a letter, drawn up by the Council, in which arguments on both sides were set forth, requesting each Fellow to consider these, and to express his opinion on the ballot paper enclosed therewith. The referendum having closed on October 1st, the scrutators reported that 1758 voting papers had been received, of which 1094 were in favour of admitting women, and 642 against the proposal, whilst 22 were neutral. Two Extraordinary Meetings of Council were devoted solely to the consideration of this result, and it was resolved, by a considerable majority, "That in the opinion of this Council it is desirable that at any time, on recommendation of three Fellows of the Society, women be accepted as Subscribers to the Society. Such women subscribers shall pay an annual fee of thirty shillings; they shall be admitted to all ordinary meetings of the Society; they shall have the same use of the Library as the Fellows, and they shall be supplied with the *Proceedings*, *Transactions*, and Annual Reports of the Society as these are issued." The considerations which led the Council to adopt this course are set forth in the statement drawn up by the Council and made by the President at the Ordinary Scientific Meeting on December 17th, 1908 (*Proceedings*, 1908, xxiv., 277).

The validity of this resolution having been called in question (*Proceedings*, 1909, xxv., 1), the terms of the resolution and of the criticisms thereon were referred to the legal advisers of the Society, Messrs. Bristows, Cooke, and Carmael, who report as follows:—

"In our opinion, the Council had power to pass this resolution. The privileges thereby proposed to be given do not in any way make women subscribers Corporators, and it was because if women were elected Fellows they would become Corporators, that Council, in April, 1904, advised they should not be elected Fellows.

"1. So far as we are aware (taking the parts of the Resolution one by one), there is nothing to prevent women subscribing an annual fee to the Society, or to prevent the Society accepting such fee. Gifts are from time to time made to the Society. The Charter provides that the Council shall have the sole management of the income and Funds of the Society.

"2. The Resolution also provides that women shall be admitted to all ordinary meetings of the Society. We understand that this has always been the custom.

"3. The Resolution next provides that the women shall have the same use of the Library as the Fellows. So far as we are aware, there is nothing in the Charter or By-Laws to prevent this, but if it is proposed that the books shall be allowed to circulate among the women Subscribers, then we think that By-Law 15 would have to be altered.

"4. Lastly, the Resolution provides that women subscribers shall be supplied with the *Proceedings*, *Transactions*, and Annual Reports of the Society as these are issued. We see nothing contrary to the Charter or By-Laws in this, and, further, we understand that any member of the public at present has this facility at prices fixed by the Council."

The triennial award of the Longstaff Medal to the Fellow of the Society who, in the opinion of the Council, has done the most to promote Chemical Science by Research, was made, on the recommendation of the Research Fund Committee, to Professor Frederick Stanley Kipping, F.R.S. The medal will be presented at the Annual General Meeting on March 25th, 1909.

The Council have regretfully accepted the resignation of Mrs. Dougal. A special vote of thanks has been accorded to Mrs. Dougal in recognition of the valuable assistance which she has rendered to the Society during the past fifteen years in indexing its Publications. Dr. C. H. Desch having resigned the position of Assistant Sub-Editor, an arrangement has been made by which all branches of the editorial work will become concentrated in the hands of Dr. Cain and Mr. Greenaway.

Following the important gift of books by Sir Henry Roscoe mentioned in the Report of the Council for 1906, the munificence of the same donor has enriched the Library with a series of periodicals comprising 636 volumes. The Society is indebted also to Mrs. Sonstadt, Mr. Edward Davies, and Professor W. R. E. Hodgkinson, for the gift of valuable sets of books.

The number of books borrowed from the Library during 1908 was 1339 as against 1317 in the previous year. The additions to the Library, excluding those already mentioned, comprise 159 books, of which 90 were presented, 412 volumes of periodicals (representing 245 journals), and 36 pamphlets, as against 138 books, 401 volumes of periodicals (representing 243 journals), and 40 pamphlets last year.

In further response to the appeal of the Council referred to in the Report of last year, several Fellows have presented volumes of periodicals to help to complete the sets in the Library. The appeal has also stimulated Fellows to present to the Library a number of early chemical works. The Council welcome gifts of this description, as, in the words of Professor Emerson Reynolds, speaking from the Presidential Chair in 1902, "It is desirable that the Society should have in the Library one copy, at least, of every work printed in English on chemical subjects to the end of the eighteenth century." Each of these gifts has been acknowledged in the *Proceedings* from time to time.

In consequence of the crowded condition of the Library, it has been again found necessary to construct ten book-cases in the basement; this extension, however, can afford only temporary relief.

The annual income of the Research Fund now amounts to about £346, and this year, as a fair balance was also in hand, grants amounting to £368 were made. In the *Transactions* for 1908, there are 31 papers contributed by authors who have received grants from the Research Fund.

With regard to the income and expenditure of the Society for the year just closed, there is but little calling for special comment, as both are on the same lines as those of last year. The total income for 1908 is £7134 17s. 2d., which is less than that of the previous year by £125 7s. 8d.; the expenditure is £6834 15s., or only £84 6s. 7d. more than that of last year. This leaves an excess of £300 2s. 2d. of income over expenditure for the year's working, as compared with £509 16s. 5d. for 1907, and £741 13s. 2d. for 1906. It may seem somewhat remarkable that, with an increase of 50 in our list of Fellows, we should have a smaller income from admission fees and from annual subscriptions, which are the items in which there is the most notable falling off. This is, however, accounted for by the large number elected in November and December, whose subscriptions and admission fees do not become due until January 1st, 1909, and therefore do not appear as arrears in the 1908 account, but will swell the income for 1909. This will be welcome to the Treasurer, for the preparation for Vol. V. of the Decennial Index (which has even now begun) must be actively proceeded with by our Editor under the arrangements just concluded. The *Journal* has cost £192 2s. 6d. more than last year, but a saving of £37 15s. 6d. has been effected on the *Proceedings*. Administrative expenses are £54 5s. 4d. less than last year, due to our economies in several directions being greater than increased expenditure in others, but the total effect has been to secure greater efficiency. It is obvious, however, that unless authors will actively aid the Publication Committee in their endeavours to keep down the continual increase in the cost of the *Journal*, it will be

necessary to raise the annual subscription from £2 (which it has been ever since the foundation of the Society) to £2 10s.

Dr. DIVERS having given due notice that he would move the adoption of the following new By-Law:—

XIII. *bis*.—On Ascertaining the Will of the Society by means of Voting Papers.

"The President, either on his own motion or on a written requisition by the Council or by fifty Fellows, shall proceed to ascertain the will of the Society as to any suggested change in the By-Laws or in the administration of these laws by the Council, by causing to be delivered, along with the *Proceedings* or separately, a notice to each Fellow of the change proposed, together with a voting paper upon it, to be filled in by the Fellow and returned to the Secretaries not later than a prescribed date. After that date, the results of the voting shall be counted by the Secretaries and two Scrutineers, appointed by the President, and be reported by him to a Council Meeting and to a General Meeting, upon which the Council shall proceed to act in accordance with the majority of votes, as being the expression of the will of the majority."

the President declared that his duty prevented him from putting the proposition to the Meeting, the suggested By-Law being repugnant to the Charter. Dr. DIVERS then withdrew his Resolution, and gave notice that at a subsequent General Meeting he would propose the By-Law so amended that the word "may" replace the word "shall."

The PRESIDENT then presented the Longstaff Medal for 1909 to Prof. F. S. KIPPING, who responded in terms expressing his appreciation of the honour bestowed upon him.

A vote of thanks to the Treasurer, Secretaries, Foreign Secretary, and Council for their services during the past year was proposed by Dr. L. T. THORNE, seconded by Dr. McGOWAN, and acknowledged by Prof. H. E. ARMSTRONG.

The PRESIDENT then delivered his address, entitled "Elements and Electrons." Prof. J. J. DOBBIE proposed a vote of thanks to the President coupled with the request that he would allow his address to be printed in the Society's *Transactions*, the motion being seconded by Prof. F. S. KIPPING, and acknowledged by the PRESIDENT.

The Scrutators having presented their report, the PRESIDENT declared that the following had been elected as Officers and Council for the ensuing year.

President.—Harold B. Dixon, M.A., F.R.S.

Vice-Presidents who have filled the office of President.—H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, D.Sc., F.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; A. Vernon Harcourt, M.A., D.C.L., F.R.S.; Raphael Meldola, F.R.S.; H. Muller, Ph.D., LL.D., F.R.S.; W. Odling, M.A., M.B., F.R.S.; Sir William Ramsay, K.C.B., LL.D., F.R.S.; J. Emerson Reynolds, Sc.D., M.D., F.R.S.; Sir Henry E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; T. E. Thorpe, C.B., LL.D., F.R.S.; W. A. Tilden, D.Sc., F.R.S.

Vice-Presidents.—J. Campbell Brown, D.Sc., LL.D.; J. Norman Collie, Ph.D., F.R.S.; J. J. Dobbie, M.A., D.Sc., F.R.S.; F. Stanley Kipping, D.Sc., Ph.D., F.R.S.; Sir Alexander Pedler, C.I.E., F.R.S.; James Walker, D.Sc., Ph.D., F.R.S.

Treasurer.—Alexander Scott, M.A., D.Sc., F.R.S.

Secretaries.—M. O. Forster, D.Sc., Ph.D., F.R.S.; A. W. Crossley, D.Sc., Ph.D., F.R.S.

Foreign Secretary.—Horace T. Brown, LL.D., F.R.S.

Ordinary Members of Council.—Julian L. Baker; George T. Beilby, F.R.S.; William A. Bone, D.Sc., Ph.D., F.R.S.; Alfred C. Chapman; Julius B. Cohen, Ph.D., B.Sc.; Charles E. Groves, F.R.S.; J. T. Hewitt, M.A., D.Sc., Ph.D.; W. R. E. Hodgkinson, Ph.D.; H. R. Le Sueur, D.Sc.; G. T. Morgan, D.Sc.; A. G. Perkin, F.R.S.; A. E. H. Tutton, M.A., D.Sc., F.R.S.

Anniversary Dinner.

The Anniversary Dinner of the Society was held at the Whitehall Rooms, Hotel Metropole, on Thursday, March 25th, 1909.

The Royal Toasts having been duly honoured, Sir HUGH BELL, Bart., President of the Iron and Steel Institute, in proposing the "Chemical Society," coupled with the name of The PRESIDENT, said that no branch of human industry owed a greater debt to the science which that Society had been formed to promote than the Iron and Steel Trade. In every branch of that industry, chemical science was continually assisting, and without it they would be unable to conduct those intricate operations which resulted in such a large measure of well-being to the human family. Even to battleships, of which so much had been heard of late, the President had contributed not a little, but he, Sir Hugh, preferred to emphasise the peaceful side of their industry, and their gratitude to chemistry and the President of the Chemical Society was rather for having promoted peace, not warfare. It was a science which, if properly used, might be largely instrumental in the education of the youth of our country. Of all the sciences, chemistry was that one which compassed most completely the true objects of experimental science, seeking always for its verification the repetition of the phenomena under investigation. It too frequently happened, however, that what was called chemical instruction was merely a "messaging about" with test-tubes which did no good to any living soul. If it were indeed necessary to exclude all test-tubes from technical departments—even if they had thereby to exclude chemistry itself—they might be doing something of real benefit to education.

Sir WILLIAM RAMSAY, in responding to the toast, reviewed in an interesting manner the chief events associated with the Society since his entrance into the Society in 1873. He gave a number of interesting and amusing reminiscences of many of the pioneers of modern science with whom he had come into personal contact. Alluding to the inutility of examinations in testing the ability of chemists, he regarded such examinations in the light of a necessary evil. They were inadequate to gauge the abilities of a chemist, which depended upon other mental qualities than readiness, quick-wittedness, and good memory. The latter were undoubtedly useful qualities, but what the chemist more particularly required was the power to obtain accurate results by means of long-continued thought and careful observation. The Chemical Society was expanding in its influence at home and abroad, and had now nearly 3000 Fellows, and had children and grandchildren in the form of chemical societies practically everywhere, but more especially in the Colonies and the United States. He could not venture to predict what the future of chemistry might be. The days of the Admirable Crichton were gone, and it was now impossible to be proficient in all branches of human knowledge. It was therefore more necessary than ever that the chemist should know something about everything in chemistry and everything about some particular branch of it. There was an overwhelming output of chemical knowledge, and it was hopeless to attempt to read all the books published nowadays. His advice to authors of works on chemistry was to reduce them to the irreducible minimum, taking care to be lucid, concise, and sufficiently comprehensive. One aim of the Society should be to promote courses of lectures, summing up particular subjects so as to extend the general knowledge of chemistry. This was very essential, as owing to the accumulation of detail, specialisation was very necessary, but the disadvantage of this was that persons were apt to have no great knowledge of, or interest in, the work of those engaged in other branches of their science. Chemistry was becoming more and more essential in all branches of life, and exercised a great influence in war and peace. That influence would increase, and he had no doubt that the Chemical Society would flourish in the future as it had done in the past.

Prof. RAPHAEL MELDOLA, Past President of the Chemical Society, proposed the toast of "The City and Guilds of London," coupled with the names of Mr. F. A. Roberts, Master of the Worshipful Company of Grocers, and Mr. Walter S. Gardner, Master of the Worshipful Company of Drapers. It was a popular belief, declared Prof. Meldola, that City Companies were associated solely with City banquets and gorgeous palaces. As a servant of those Companies taking cognisance of what was going on in the upper regions, he could assure them that the holding of banquets was not their sole object of existence. We were perhaps familiar with their efforts in the cause of charity, but he wished to allude to the assistance they gave to the cause of education and science. It was thirty years since the cry of "Technical Education" was raised in this country. That cry meant that there was not a sufficiently close association between science and industry. The City and Guilds threw themselves into the breach, and boldly undertook the pioneering work of technical education in this country. They took over the work that the State had not touched hitherto, and the foundation of the City and Guilds of London Institute was the outcome; and during the period from 1878 to 1908, fifty two City Companies contributed to that Institute £768,360 to advance the cause of British technical education.

Mr. F. A. ROBERTS, responding for the Worshipful Company of Grocers, reciprocated the kindly sentiments of Professor Meldola. The Company were prepared to continue their good work, but hoped that there would be no outside interference with them, as he believed they were employing their money to the best interests of science, education, and charity.

Mr. WALTER S. GARDNER responded for the Worshipful Company of Drapers, and referred to the useful work of their Company in the matter of apprentices, a work which they hoped would mitigate to some extent the evil of sending boys out at an early age to earn a few shillings a week for three or four years, after which they become practically unfit for anything of service to the community.

Prof. H. A. MIERS, proposing the toast of "Scientific Societies," coupled with the name of Sir Archibald Geikie, President of the Royal Society, said the tendency was for Societies to go on multiplying and specialising. The work of specialisation was becoming so serious that the fear was that when a paper was read at a scientific society nowadays, the only person who at all understood it was the author himself. Perhaps such a circumstance had its own field of usefulness, and he reminded them of the man who left £10,000 in his will to the Society whose meetings had proven such an excellent antidote to insomnia. He hoped that some method could be found to make use of the splendid amateur materials of which the various scientific societies consisted. Whether the societies were making the best use of their opportunities or not, there was one extremely wholesome sign about their present state—they were in no danger of becoming a Joint Mutual Admiration Society, but were living in the bracing atmosphere of criticism which was undoubtedly useful in the promotion of their work as a whole.

Sir ARCHIBALD GEIKIE, in response, said that science had grown enormously of late. There was the danger, as the President had pointed out, that specialisation would go on so far that the votary of one branch of science should be entirely unacquainted with what was taking place in another branch of it. It was a very bad thing, he declared, for a man to live in water-tight compartments of knowledge. It would enlarge his views if he took in something from other spheres of knowledge. Something, he was glad to say, was being done in that direction, and none of the societies moving that way had attained greater success than the Chemical Society.

Prof. J. EMERSON REYNOLDS proposed the toast of "The Guests," and alluded in warm terms to Lord Balfour of Burleigh and Sir James Crichton-Browne, whose names were coupled with the toast.

Lord BALFOUR OF BURLEIGH responded as the unworthy

representative of the Church, which had disappeared, of the law which was still worthily represented, and of various educational authorities whom he saw before him, and to whom he had been in servitude on former occasions.

Sir JAMES CRICHTON-BROWNE, also responding to the toast of "The Guests," said it was delightful to know that the members of the Royal Family, including His Majesty the King, were showing a great and intelligent interest in the work of the Royal Institution, which he, Sir James, represented. That interest was being extended to the forthcoming Congress at the Albert Hall. As to the general outlook, we had fallen upon lean years. We had with us unemployment and sombre anticipations of the next Budget. We look to the chemists for new knowledge which should not only enable us to redress some of the evils we saw around us, and, in a utilitarian sense, largely add to the comfort and convenience of human life, but which, better still, should make for the clarification of our conceptions of the Universe, and for the refinement and ennobling of our lives.

ROYAL INSTITUTION.

Annual Meeting, May 1st, 1909.

Sir JAS. CRICHTON-BROWNE, Treasurer and Vice-President, in the Chair.

THE Annual Report of the Committee of Visitors for the year 1908, testifying to the continued prosperity and efficient management of the Institution, was read and adopted, and the Report on the Davy-Faraday Research Laboratory of the Royal Institution, which accompanied it, was also read. Forty-eight new Members were elected in 1908. Sixty-three Lectures and nineteen Evening Discourses were delivered in 1908. The books and pamphlets presented amounted to about 238 volumes, making, with 708 volumes (including periodicals bound) purchased by the Managers, a total of 936 volumes added to the Library in the year.

Thanks were voted to the President, Treasurer, and the Honorary Secretary, to the Committees of Managers and Visitors, and to the Professors, for their valuable services to the Institution during the past year.

The following gentlemen were unanimously elected as Officers for the ensuing year:—

President—The Duke of Northumberland.

Treasurer—Sir James Crichton-Browne.

Secretary—Sir William Crookes.

Managers—Sir Thomas Barlow, Bart.; William Phipson Beale, M.P.; Horace T. Browne; The Rt. Hon. Sir Henry Burton Buckley; Charles Hawksley; Dr. Donald William Charles Hood; Alfred B. Kempe; The Rt. Hon. Lord Kinnaird; Sir Francis Laking, Bart.; Henry Francis Makins; George Matthey; Rudolph Messel; The Rt. Hon. Sir John Fletcher Moulton; Sir Andrew Noble, Bart.; and The Hon. Lionel Walter Rothschild, M.P.

Visitors—Dr. William Arthur Brailey, Arthur N. Butt, James Mackenzie Davidson, Richard T. Glazebrook, John William Gordon, Dr. James Dundas Grant, Major-General Sir Coleridge Grove, Charles Edward Groves, John List, Sir Philip Magnus, Robert Mond, Colonel Sir Frederick Nathan, The Hon. Charles A. Parsons, James Swinburne, and Arthur James Walter.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 3rd inst.; the Duke of Northumberland, K.G., President, in the Chair. Dr. H. S. Collier, Mr. J. Benson Kennedy, Prof. H. A. Miers, Mr. T. P. Warren, and Sir Almroth E. Wright were elected Members. The Chairman announced that he had appointed the following Vice-Presidents for the ensuing year:—Dr. Donald W. C. Hood, Mr. A. B. Kempe, Sir Francis Laking, Bart., Mr. George Matthey, The Rt. Hon. Sir John Fletcher Moulton, Sir Andrew Noble, Bart., Sir James Crichton-Browne (Treasurer), and Sir William Crookes (Honorary Secretary).

NOTICES OF BOOKS.

Elementary Agricultural Chemistry. By HERBERT INGLE, B.Sc. London: Charles Griffin and Co., Ltd. 1908.

As a handbook for the agriculturist who knows no chemistry this work has some good features. The difficulties of giving practical men any real insight into the foundations of chemical science are very nearly insuperable when the attempt is made, as in this book, to compress the necessary information into one short introductory chapter. However, the author impresses upon his readers the necessity for consulting a text-book of general chemistry, and devotes his energy more particularly to the applications of the science to agriculture. In the chapter on the nature of soils the movement of water in the soil is well treated. The discussion of the composition of manures is well up to date, while the chapters on the life of the plant, the feeding value of various materials, &c., are practical and, for the size of the book, complete. Some useful notes are added on the chemistry of insecticides, disinfectants, and other miscellaneous agents. For the prospective colonist the book has some value, for the practice of countries other than England is not neglected; thus, some account is given of the agricultural methods which are generally adopted in South Africa.

First Principles of Chemical Theory. By C. H. MATHEWSON, Ph.D. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1908.

THE author of this book may be congratulated upon having most successfully evaded the danger of producing a sketchy and more or less inaccurate outline of the leading principles of chemical theory in a presentation of the subject which is very simple and brief. The book may be said to have two distinct uses; for beginners it gives a clear review of theoretical principles, quite sufficient for the candidate for, say, the matriculation examination of the University of London, and although in some ways it goes a good deal beyond the syllabus of this particular examination, this is by no means a disadvantage. The short discussions of the Law of Chemical Mass Action and the Phase Rule are not at all too difficult for the average student at this stage in his work, and by most they will be found to be most illuminating and interesting. Moreover, the book will be found valuable by the more advanced student, to be used as a sort of skeleton round which to build up a more extended knowledge of the theory of chemistry, which may be acquired from larger and more specialised works. Given a really satisfactory outline, this method of studying the general principles of the science should be the best that can be adopted, for all haziness upon fundamentals is thus made practically an impossibility. Only a really admirable elementary text-book can, however, be used successfully in this way, and this book can be recommended with confidence as specially suitable for the purpose.

Laboratory Notes on Industrial Water Analysis. By ELLEN H. RICHARDS. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1908.

SPECIAL methods of determining whether samples of water are suitable for use in boilers and for general engineering purposes are described in the laboratory exercises given in this book. Ordinary analytical processes for testing water are not treated. Waters are divided into four classes:— I. Those which are scale-forming. II. Those which are moderately scale-forming. III. Corrosive waters which are not scale-forming. IV. Waters containing considerable amounts of sodium salts. Methods of ascertaining to which class a given sample belongs are given, and the action of corrosive waters on common metals is shortly discussed. Some remedies for objectionable waters are described, and a short scheme is given for the testing of boiler-scale. The second part of the book contains useful hardness and other tables, and also directions for the preparation of standard solutions.

Laboratory Guide of Industrial Chemistry. By ALLEN ROGERS, Ph.D. London: Archibald Constable and Co., Ltd. 1908.

ANY book which aims at bridging over the gap between factory and laboratory, and between the works chemist and the student, may be almost sure of being well received, and there is a good deal to be said for the plan of giving the technical student an insight into the processes concerned in other industries than that in which he hopes to specialise. In many ways this book is worth the study of demonstrators and instructors in technical schools and colleges, and though not without faults it should certainly be found helpful by those engaged in the teaching of industrial chemistry. The industries treated include dyeing, paints and varnishes, soaps, paper, and leather, the first being treated at the greatest length. In fact, in this subject there is rather a multiplication of exercises which are not always typical. In addition some space is somewhat unnecessarily given up to directions for the preparation of important inorganic and organic substances. The demonstrator could very readily pick out from a work on general practical chemistry such preparations as would be suitable, and, indeed, most students would have performed a good many of the experiments in their preliminary work. The directions given in the book only differ from those in an ordinary practical book in suggesting the use of rather larger quantities of ingredients, and also in recommending the student to estimate the cost per pound of the substance in question.

Die Stearinfabrikation. ("The Manufacture of Stearin"). By Dr. Phil. BELA LACH. Halle-a-S: Wilhelm Knapp. 1908.

THIS book may almost be described as an amplification of the author's monograph on the manufacture of glycerin, and resembles it in many respects. It is marked by the same thoroughness, and aims at giving special prominence to practice and passing over theory. It contains detailed descriptions of many typical modern factories, accompanied by drawings and plans; not unnaturally German methods are considered more fully than those which are employed in other countries. The applications and uses of stearin are shortly treated in an appendix, and a very brief account is given of the simplest and quickest way to determine the free fatty acids in mixtures of fats. No attempt is made to discuss the analysis of fats in general, but the summary of results obtained with fats of different origin and composition will be found a useful feature of the book.

The Geology of the Goldfields of British Guiana. By J. B. HARRISON, C.M.G., M.A., F.I.C., F.G.S. London: Dulau and Co. 1908.

THIS volume may be regarded as the official report on the geology of British Guiana, having been published by the direction of the Governor, Sir Frederic M. Hodgson, K.C.M.G. It contains a systematic account of the petrography of the various rocks found in different districts, with excellent microphotographs of sections of typical specimens. The descriptive geology of the colony is also treated fully, and is illustrated with photographs of places which are interesting from a geological point of view. The structures and soils of the auriferous areas are described in detail, and the book concludes with practical hints to intending miners and prospectors on such subjects as transport facilities, labour, &c. The laws and regulations governing the mining industry are given in an appendix.

Laboratoriumsbuch für die Erdöl Industrie. ("Laboratory Book for the Petroleum Industry"). By Dr. RICHARD KISSLING. Halle-a-S.: Wilhelm Knapp. 1908.

THIS book is the companion volume to the author's monograph on the preparation and uses of petroleum belonging to the series of monographs on technical chemical manu-

factures issued by the same publishers. It describes the most important methods used in practical work, purposely avoiding a great choice of processes, while at the same time giving full information for the qualitative and quantitative investigation of petroleum. The different types of apparatus in use for determining flash-point, viscosity, &c., are carefully explained, and the use of them is adequately treated. Some details of the testing of substances which are employed in the refining of petroleum will be found of value. The absence of an alphabetical index is a drawback even to a book of this size.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlviii., No. 12, March 22, 1909.

Experimental Study of the Coefficient of Distribution and its Application to the Volatile Acids of Wines.—Philippe Malvezin.—By applying Berthelot and Jungfleisch's rules and determining the ratio p'/p of the quantity of volatile acids dissolved by ether and water, the author finds that it is possible to ascertain very rapidly the volatile acidity of wines. The solubility of these acids in sulphuric ether at 65° is found, remembering that they dissolve in the proportion 72 : 100. This method is very rapid and exact, and no distillation is required.

New Method of Preparing the β -Halogen Derivatives of Naphthalene.—G. Darzens and E. Berger.—When the halogen derivatives of phosphorus act on the sodium compounds of alcohols and phenols, phosphorous and phosphoric ethers are formed and also hydrochloric ethers. This reaction can be applied to sodium β -naphthol, and the product is β -brom or β -chlor-naphthalene. The yields are good, the trihalogen phosphorus compounds giving the best results.

Rôle of Magnesia in the Transformation of Saccharose at Different Temperatures.—J. Tribot.—In experiments of short duration the transformation of saccharose begins to become stationary with diastase containing magnesia at 40°, while it continues to increase up to 60° with diastase and no magnesia. The influence of diastase purified by successive precipitations and giving only an imponderable mineral residue is not zero, though much diminished. At high temperatures more saccharose is transformed in the same time by diastase with magnesia than by diastase without magnesia.

MEETINGS FOR THE WEEK.

MONDAY, 10th.—Royal Society of Arts, 8. (Cantor Lectures). "Aërial Flight," by F. W. Lancaster.

TUESDAY, 11th.—Royal Institution, 3. "Cosmogonical Questions," by Prof. Svante Arrhenius, D.Sc.

WEDNESDAY, 12th.—Royal Society of Arts, 8. "The Principles of Heredity as applied to the Artificial Production of New Forms of Plants and Animals," by Prof. A. Dendy, F.R.S.

THURSDAY, 13th.—Royal Institution, 3. "Newfoundland," by John G. Millais, F.Z.S.

Royal Society of Arts, 4.30. "Some Phases of Hinduism," by Krishna Gobinda Gupta.

FRIDAY, 14th.—Royal Institution, 9. "Solar Vortices and Magnetic Fields," by Prof. G. E. Hale, LL.D.

Physical, 8. "Bifilar Vibration Galvanometer," by W. Duddell. "Effect of Temperature on the Hysteresis Loss in Iron in a Rotating Field," by W. P. Fuller and H. Grace. "Method of Testing Photographic Shutters," by A. Campbell and T. Smith.

SATURDAY, 15th.—Royal Institution, 3. "Burke's Prose," by Prof. Walter Raleigh, M.A.

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THE CHEMICAL NEWS.

VOL XCIX., No. 2581.

REFORM OF CHEMICAL AND PHYSICAL CALCULATIONS.

By C. J. T. HANSSEN, C.E.

SINCE the year 1900 the International Table of Atomic Weights shows a constantly increasing number of elements with their atomic weights expressed in plain figures without decimals, showing that they have been found to be exact multiples of a certain unit, but with $O = 16$, H is still expressed = 1.008, and even Prof. Gustavus Hinrichs, the stout defender of $H = 1 : O = 16$, has now, after twenty years of study and exertion, adopted $O = 16 : H = 1.00781$, or $H = 1 + \pi$; where π denotes the atomic weight of the pantogen $1/128 = 0.00781$ of H .

In determining the weight of the pantogen, Prof. Hinrichs has surely made a grand and important discovery; the pantogen, the universal substance of which the atoms of elements and heavenly spheres are built, and which fills all

THE MUNROE CRUCIBLE.

By WALTER O. SNELLING.

THE use of platinum felt as the filtering medium in a crucible of the Gooch pattern was first suggested by Charles E. Munroe, in an article entitled "Filtration with Filters of Metallic Felt," published in the *Journal of Analytical Chemistry*, vol. ii., July, 1888 (and reprinted, CHEMICAL NEWS, 1888, lviii., 101).

Crucibles prepared by the method suggested by Munroe have many advantages not possessed by any other type of apparatus used for filtration, and since the use of such crucibles is by no means as general as their merit would warrant, it seems desirable to again briefly describe the preparation and uses of crucibles of this type.

Preparation of the Munroe Crucible.—A concentrated solution of chlorplatinic acid is precipitated by ammonium chloride, the latter reagent being added in slight excess. The resulting precipitate of ammonium platonic chloride is washed several times with water, and is finally washed with alcohol, the excess of alcohol being poured off as soon as the ammonium chlorplatinate has settled. A perforated platinum crucible (one preferably in which the perforations are numerous and small) is then placed upon several layers of filter-paper, and held firmly in this position

Authority.	Weight of 1 litre. Mgrms.	Weight of π . Mgrms.	Weight of 1 litre pure. Mgrms.	Atomic weight.
<i>At Latitude 45°, Sea-level, $\pm 0^\circ C.$, 760 mm. Barometer.</i>				
Rayleigh	$O = 1429.050$	$- 0.697$	$= 1428.353$	$O = 16$
	$H = 89.980$	$- 0.697$	$= 89.283$	$H = 1.0002$
	$N = 1250.700$	$- 0.697$	$= 1250.003$	$N = 14.002$
	$C = 1071.750$	$- 0.697$	$= 1071.053$	$C = 11.9977$
Morley	$O = 1429.000$	$- 0.697$	$= 1428.303$	$O = 16$
	$H = 89.993$	$- 0.697$	$= 89.296$	$H = 1.0003$
Berthelot	$O = 1429.200$	$- 0.697$	$= 1428.503$	$O = 16$
	$H = 89.986$	$- 0.697$	$= 89.289$	$H = 1.00007$
Reform	$O = 1429.777$	$- 0.697$	$= 1429.080$	$O = 16$
	$H = 90.015$	$- 0.697$	$= 89.318$	$H = 1$
	$N = 1251.150$	$- 0.697$	$= 1250.453$	$N = 14$
	$C = 1072.515$	$- 0.697$	$= 1071.818$	$C = 12$
<i>At Latitude 41° 10', Circle of International Gravity, Sea-level, $\pm 0^\circ C.$, 759.724 mm. Barometer.</i>				
Reform	$O = 1429.267$	$- 0.697$	$= 1428.570$	$O = 16$ 1 litre of pure gas weighs 80/56 grms.
	$H = 89.9827$	$- 0.697$	$= 89.2857$	$H = 1$ " " 5/56 "
	$N = 1250.697$	$- 0.697$	$= 1250.000$	$N = 14$ " " 70/56 "
	$C = 1072.125$	$- 0.697$	$= 1071.428$	$C = 12$ " " 60/56 "

the empty spaces between atoms and between suns and planets, can and must now be taken into account for chemical and physical experiments and calculations. The writer of these lines has carefully studied this matter, and has, in Prof. Hinrichs' discovery, found the means to prove that the atomic weights of the elements are *exact multiples* of the of the atomic weight $H = 1$, and that the proportion $H = 1 : O = 16$ is absolutely correct, and that my "Reform of Chemical and Physical Calculations" is built upon a solid and correct foundation.

Lord Rayleigh (at 45° lat., sea-level, $0^\circ C.$, 76 mm.)—
1 litre $H = 89.98$ mgrm.

Prof. G. Hinrichs' pantogen, $\pi = H/128$,—

$$1 \text{ litre } \pi = \frac{89.98}{128} = 0.697 \text{ mgrm.}$$

One litre of any gas or other elementary substance contains, besides its atoms of pure substance, 1 litre = 0.697 mgrm. of π .

To find the *exact* atomic weight of 1 litre pure gas substance, deduct 0.697 mgrm. π from the weight, ascertained by weighing the gas. (See Table).

Copenhagen, V., March 30, 1909,
Valdemarsgade 3.

while the alcohol-moist mass of ammonium chlorplatinate is poured into it, usually until it is filled to a height of from 0.25 to 0.5 cm. The alcohol will be rapidly absorbed by the filter-paper upon which the crucible is pressed, and at the expiration of a few moments the surface of the salt in the crucible will show that all of the excess has been taken up by the filter-paper, the crucible being held firmly against the layers of filter-paper until this occurs. The moment at which the last of the excess of alcohol is absorbed by the filter-paper is readily noted by the sudden "drying" of the surface of the ammonium chlorplatinate which takes place at that instant.

The crucible can now be removed from the filter-paper, and if the foregoing operations have been properly performed, an even layer of ammonium chlorplatinate will be found to cover the bottom of the crucible, the filter-paper having prevented any from having run out through the perforations. The crucible is now warmed in a water-oven until the alcohol has been entirely driven out of the salt, and then, after the cap and cover have been put on, the crucible is slowly and cautiously heated until the decomposition of the ammonium chlorplatinate is effected, the heating being continued until the crucible reaches dull redness.

When the crucible cools it will be found that a layer of coherent platinum sponge covers the bottom, this layer being sometimes continuous and evenly covering the bottom of the crucible, but more often it will be interrupted by several cracks, and drawn away from the sides of the crucible. By gently pressing with the finger or with a glass rod flattened somewhat at the end, the platinum sponge can be pressed together at the places where cracks have appeared, and, if carefully done, a continuous layer of platinum sponge can thus be formed over the entire bottom of the crucible. If, however, the trial has not been successful in preparing a thoroughly continuous layer, fresh chlorplatinic acid can be used to fill up the cracks and "patch" the platinum sponge layer, or the entire layer can be removed by means of a spatula, and the trial repeated until an even coherent layer of platinum sponge completely covers the bottom of the crucible. When this has been achieved the crucible is finished.

Characteristics of the Munroe Crucible.—Prepared as described, the mat of the Munroe crucible forms a smooth, even layer, of light silver-grey colour over the bottom of the crucible. To the touch the mat presents the soft and slightly elastic feeling characteristic of metallic felts.

The porosity of the mat, and at the same time its ability to retain the finest precipitates, are factors so marked as to cause surprise to one who uses the crucible for the first time. Experiments were tried by the writer to determine the relative porosity of crucible filters with asbestos, and with platinum felt, as the filtering medium, the experiments being carried out as follows:—A rubber stopper was selected of such size that it would just fit into the top of the crucible, and through a perforation in this stopper the lower end of a glass tube somewhat over a metre long was placed, the upper end of this tube being so bent as to syphon from a large vessel of water placed upon an elevated shelf. The height of water in the vessel was such that the vertical distance from the level of the water to the bottom of the crucible was just one metre. Directly under the crucible a 500 cc. graduated flask was placed, and the length of time required by the different crucible filters to allow 500 cc. of distilled water to pass was noted.

The first crucible tested was one with asbestos mat, taken at random from a number of crucibles which had been made up for general work, and with no intention of being subjected to test. 25.6 minutes were required for 500 cc. water to pass. A Munroe crucible was next taken and 500 cc. of distilled water were found to pass in four and three quarter minutes, the platinum felt mat thus being seen to have a porosity five times as great as the asbestos mat. About these same relative figures were obtained in all the experiments tried, eight crucibles with asbestos mat, and five with platinum felt mat, being tested, the average time required to pass 500 cc. of water being five and a-quarter minutes in the case of crucibles with the platinum felt mat, and thirty-one and a-half minutes in the case of the crucibles with asbestos mat. As the average amount of asbestos used in each crucible was 0.145 gm., and the average weight of the platinum felt mat was 0.4400 gm., it will readily be seen that weight for weight the porosity of platinum felt is more than a hundred times as great as asbestos felt.

The platinum felt retains without difficulty the finest precipitates, and many substances which cause trouble when filtered in the ordinary Gooch crucibles using asbestos are easily filtered in the Munroe crucible. Barium sulphate and calcium oxalate can be collected by the platinum felt mat without the filtrate even being clouded the first time running through (*Geo. Wash. Bull.*, 1906, vol. v., No. 4, p. 82).

Uses of the Munroe Crucible.—In the platinum felt crucible not only the body of the crucible, but the filtering medium as well, is platinum. The advantage which platinum has through its almost absolute insolubility in nearly all laboratory reagents has made it indispensable to the chemist, and through the use of the Munroe crucible the advantage gained by the use of platinum is extended

to the apparatus used in filtration. Even with the use of platinum dishes the chemist must bear in mind the slight solubility effect of certain reagents, and of course this same care must be taken to protect the platinum felt crucible from these substances. With this fact in mind, and with careful handling, the platinum felt crucible will be found to cover practically all the requirements of a crucible filter. In the ordinary crucible filter, using asbestos as a filtering medium, traces of silica, magnesium, iron, and aluminium will sometimes be found to be dissolved from the asbestos and to contaminate the filtrate. While it is true that this happens but seldom, and usually in such small amount that no serious harm is done, yet it is also true that after certain chemical operations the decomposition of the asbestos becomes quite marked, so that very appreciable errors can be quite easily brought about, and in exact chemical work even the ordinary slight solvent action upon the asbestos is detrimental to the accuracy of the work, or requires tedious separations and blank determinations. With the Munroe crucible the body of the crucible and the filtering medium are composed of but a single element, and consequently but a single impurity can be introduced in the process of filtration; while by the use of care in the work, and the choice of suitable reagents, the possibility of platinum being carried away becomes extremely remote. One case only requires particular mention; platinum sponge is known to be slightly soluble when acted on by hydrochloric acid in the presence of air or oxygen, and accordingly platinum felt crucibles which have just been used in the filtration of hydrochloric acid solutions should be washed with water thoroughly before being dried.

By the choice of an appropriate solvent, the precipitate which has been collected in the Munroe crucible can be dissolved, leaving the crucible ready, after drying and weighing, for the next determination, the crucible thus being used over and over, a new mat only being prepared when careless handling makes this necessary. A crucible used by the writer has now served in about two hundred analyses of the most varied nature and is still in good condition, the mat never having had to be changed in any way.

In dissolving the precipitates which have been collected in the crucible, particularly in the case of carbonates, through the effervescence of which, on contact with acid, particles of the mat are likely to be dislodged, it is desirable to place the crucible in a pipe-stem triangle over a porcelain dish (Thesis of M. M. Brewer, Geo. Washington University, 1901, p. 28), so that the bottom of the crucible is immersed in a dilute solvent placed in the dish. By gradually heating the solvent, not quite to boiling, the precipitate can be quickly dissolved.

Although the platinum felt crucible is admirably adapted to nearly all the varied requirements of a crucible filter, it seems to the writer that it is in the determination of atomic weights, and similar work requiring extreme accuracy, it has its best field of application. Richards and Staehler have used the Munroe crucible with success in their work on the atomic weight of potassium (*Journ. Am. Chem. Soc.*, 1907, xxix., 623), finding in it an instrument well adapted to their needs in that work, and it is probable that the substitution of the Munroe crucible for crucibles with asbestos felt, in most atomic weight determinations, would be found to be advantageous.

The use of the Munroe crucible in the determination of reducing sugars has been described by Pelet (*Bull. Assoc. Chim. Sucr. Dist.*, xxiv., 1392), and by Zerban and Naquin (*Journ. Am. Chem. Soc.*, 1908, xxx., 1456). Gooch and Beyer, in their work on the use of filtering crucibles in electrolytic analysis, have recently pointed out advantages which can be gained in certain cases through the use of platinum felt as the filtering medium (*Am. Journ. Sci.*, 1908, xxv., 249).

Pelphs has used the Munroe crucible in his work on the analysis of barium sulphate, and has found that results difficult or impossible to reach by the use of crucibles con-

taining asbestos mats can be easily obtained by the use of the platinum felt crucible.

General Notes.—In his original paper (*Journ. Anal. Chem.*, 1888, ii., 241) Munroe refers to rubbing the platinum sponge with a glass rod to smooth out the mat and remove cracks, and this procedure compresses the mat and burnishes its surface to a considerable degree. By gently rubbing all parts of the mat with some hard object until the surface becomes considerably burnished, a very smooth and polished surface is obtained, which for some purposes becomes of considerable advantage, although it should be noted that the porosity of the felt is greatly diminished.

In preparing platinum felt crucibles, advantages can be gained by placing a circular piece of fine platinum wire gauze of suitable size in the bottom of the crucible, before pouring in the ammonium platonic chloride, the mat being tougher and less easily injured, and also being less liable to crack and curl when it has the support of the skeleton formed by the platinum gauze.

Precipitates often cling very tenaciously to the surface of the platinum felt, and if removed mechanically will often take particles of the felt with them. In cases where it is necessary to mechanically remove precipitates, the method suggested by Richards and Staehler (*Journ. Am. Chem. Soc.*, 1907, xxix., 623), of placing a perforated disk of platinum of suitable size on the top of the layer of platinum sponge, will be found to be of advantage.

If two or three drops of chlorplatinic acid are placed upon the platinum felt mat in a crucible, the porosity of the felt will cause the solution to distribute itself through the mat, and if the crucible is then ignited the chlorplatinic acid will be decomposed with the separation of platinum. It is probable that the platinum thus separated within the body of the mat cements the particles of platinum sponge together to a certain degree, and also cements the sponge to the body of the crucible (and to the platinum gauze, if such has been used), so that when so treated the felt mat is somewhat toughened.

Several names have been used by previous writers in referring to crucibles with platinum felt as the filtering medium. Munroe in his original publication refers to his device simply as "Filters of Metallic Felt," and other writers have used the name "Gooch-Munroe" (*Journ. Am. Chem. Soc.*, 1907, xxix., 633) and "Munroe-Neubauer" (*Ibid.*, 1908, xxx., 1456) crucible. The writer sees no necessity for this hyphenation, since Munroe has undoubtedly priority in the use of platinum felt as a filtering medium in a filtering crucible, in all the three elements which are involved in the conception and presentation to science of an idea; viz., invention, experimentation, and published description, and accordingly the only name which seems suitable is that used as the title of this article.—*Journal of the American Chemical Society*, xxxi., No. 4.

"BENNETT BROUGH" MEMORIAL FUND.

ON the lamented death of Mr. Bennett Brough, Secretary of the Iron and Steel Institute, the Members raised a fund for the assistance of his widow and children. The response was a liberal one, about £6000 being subscribed, and this fund is now closed.

Many of Mr. Brough's friends who had no opportunity of subscribing to the above fund have expressed a desire to establish a lasting memorial, which it is suggested should take the form of a scholarship for boys from the City of London School, where he was educated, tenable at the Royal School of Mines, where both as Student and Teacher he did such excellent work.

An influential Committee has been formed for the purpose of carrying out this object, the Treasurer being Mr. R. E. Commans, Speer Road, Thames Ditton, Surrey, and it is hoped that many readers of the CHEMICAL NEWS, who knew and appreciated the sterling qualities of Mr. Brough, will subscribe to the fund.

Mr. Brough's personality and tact endeared him to all, and although most were aware of his kindly thought for others, but few knew of the constant quiet help and sound advice for which his friends, and even those who were little more than acquaintances, were indebted to him.

The loss to the scientific world by the death of Mr. Brough in his forty-eighth year, and at a time when his work, always appreciated, was of still increasing value to the community, can scarcely be estimated, and those who knew him best can alone realise the impossibility of filling the many honorary and other positions whose duties he so ably carried out.

Few were better known and none were more respected, and his death leaves many blanks both in public departments and in the lives of his friends.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, April 29th, 1909.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

"Note on the Results of Cooling certain Hydrated Platinocyanides in Liquid Air," by J. EMERSON REYNOLDS, F.R.S.

Some months ago Sir James Dewar drew the writer's attention to the fact that a colourless crystalline material, which was supposed to be lithium platino-cyanide, became temporarily red when cooled in liquid air. On repeating the experiment with some of the material which Sir James Dewar had placed in the writer's hands for examination, he found that after several repetitions of the treatment a permanent yellow substance was also formed, which did not return to the usual colourless condition at ordinary temperatures.

Chemical examination of the material led to the conclusion that it was a mixture of lithium chloride, cyanide, and sulphate, including merely a trace of platino-cyanide, but that rather less than 5 per cent of lithium platino-cyanide was present, and that the colour changes at low temperatures were due to the presence of the latter salt.

Pure lithium platino-cyanide was freshly prepared for comparison, and when analysed was found to consist of $\text{Li}_2\text{Pt}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$. The grass-green crystals of this salt did not become red when immersed in liquid air, but merely became paler in tint, therefore that salt could not be concerned in the production of the phenomena noted above.

On the other hand, pure lithium platincyanide, when fully hydrated, was shown by analysis to have the composition $\text{Li}_2\text{Pt}(\text{CN})_5 \cdot 3\text{H}_2\text{O}$. When the nearly colourless crystals of this compound were slowly cooled in liquid air they became of an intense red colour, and this change was found to coincide with the loss of one molecule of water of crystallisation, which was resumed when the temperature was allowed to rise—the colourless tri-hydrate being reproduced. Further, on rapid cooling of the tri-hydrate, a portion always passed beyond the red stage, and more or less of a yellow substance was formed. This turned out to be a yellow mono-hydrate. This hydrate also resumes water at ordinary temperatures, and affords the colourless tri-hydrate; but it was found that when certain neutral salts are present, as in the case of Sir J. Dewar's material, this re-hydration is inhibited, and the yellow mono-hydrate persists at higher temperature—hence all the phenomena noted at the outset were explained.

Similar changes of colour and composition can be effected by heating the platincyanide, but this appears to be the first case in which successive stages of dehydration of a crystallised salt have been traced on cooling the substance in liquid air.

"A Phenomenon connected with the Discharge of Electricity from Pointed Conductors." (With a Note by John Zeleny), by H. T. BARNES and A. N. SHAW.

In the study of point discharge made by Prof. John Zeleny, it was noticed that, when examined under the microscope, steel needle points, after discharging as anode, showed an irregular deposit, which extended outwards some little distance and resembled ordinary rust. A much smaller deposit was noticed when the point was made the cathode. The authors have investigated somewhat in detail the character of this deposit, not only for steel points but also for points of other metals.

Using a microscope of high power, it was possible to distinguish characteristic forms of the deposit. These the authors classify as (1) a granular deposit, (2) a tubular deposit, (3) a smooth formation, and (4) a thin film formation.

The four types are all probably connected with each other, but in appearance they are quite distinct. The tubular formation is perhaps the most interesting, and appears to be a tube of oxide growing up around a minute droplet of water, or, perhaps, hydrogen peroxide. These tubes were seen to elongate under the microscope when blown upon by moist air, and to swell up at the end as though water vapour were condensing through the thin film of oxide closing the tube. In some cases the swelling caused the oxide film to burst. In dry air the liquid appeared to recede in the tube, leaving a hard horny structure of oxide extended. The granular deposit appeared to be broken down tubes, while the smooth formation appeared to be drops of liquid with oxide so hardened as to be incapable of extension. The thin film formation was produced only on metals less easily oxidised.

The appearance of water drops on the point makes it seem probable that it is the water vapour in the discharge chamber which has condensed around the negative ions and been swept into the anode point. Discharging in absolutely dry air gave no sign of any deposit on even the most easily oxidised metals.

The slightest trace of moisture in the chamber caused a growth of deposit as much as 50 per cent of the total amount obtained when discharging in steam. The metals giving the greatest deposit were aluminium, zinc, steel, and cadmium, while gold was found to give no deposit at all.

Prof. Zeleny points out that the presence of water droplets on the point indicates a much lower temperature there than the luminosity might lead us to expect. This he verifies by making a point out of the junction of two dissimilar metals.

"On the Effect of Temperature on Ionisation," by J. A. CROWTHER.

The effect of temperature on the ionisation produced in a gas by Röntgen rays was first investigated by Perrin, who, using air, concluded that the total ionisation in a gas was independent of the temperature if the pressure were kept constant. McClung, however, who repeated these experiments later with air, carbon dioxide, and hydrogen, found that the ionisation in a gas was independent of the temperature if the density of the gas is kept constant; that is, if it is heated at constant volume.

Although no source of error could be indicated in Perrin's work, there was little doubt that the later experiments of McClung were correct, and that between the limits of his experiments (15°C. to 272°C.) and for the gases used, the ionisation produced by Röntgen rays was independent of the temperature when the gas was kept at constant density.

It is well known that the ionisation produced by rays of given intensity in certain gases and vapours, for example, methyl iodide, ethyl bromide, or carbon tetrachloride, is much greater than that in air or carbon dioxide. The present investigation was made to discover—

(i.) If the effect of temperature on the ionisation produced in these gases and vapours were the same as for air.
(ii.) If cooling down air to a temperature near its condensation point produced any appreciable alteration in the ionisation produced in it by rays of given intensity.

As it is almost impossible to clean out completely a

vessel which has once contained organic vapours, the second experiment was performed first.

The ionisation produced by Röntgen rays has been measured in air at the temperature of liquid air, and in ethyl bromide and methyl iodide, at various temperatures up to 184°C. It was found that in every case the amount of ionisation produced was independent of the temperature of the gas, if the density of the gas remained constant.

"The Wave-making Resistance of Ships: A Theoretical and Practical Analysis," by T. H. HAVELOCK.

"On the Ionisation of Various Gases by Secondary γ -Rays," by R. D. KLEEMAN.

The ionisations of a number of gases relative to the ionisation of air by the secondary γ -rays from substances exposed to the γ -rays of radium were measured. Secondary radiators of lead, zinc, and carbon were used.

It was found that the ionisations of gases whose molecules consist of atoms of H, C, N, O, S, Cl, with the exception of H_2 , are practically the same as those obtained with the primary γ -rays. But the secondary rays produce a greater relative amount of ionisation than the primary in gases whose molecules contain atoms of higher atomic weight than that of chlorine. The ionisation of H_2 is abnormal; it is smaller with the secondary rays than with the primary.

The ionisation of the various gases, with the exception of H_2 , obey approximately an additive law. The atomic ionisations, by means of which the ionisations in the gases can be calculated, increase more rapidly with the atomic weight with the secondary rays than with the primary.

CHEMICAL SOCIETY.

Ordinary Meeting, April 1st, 1909.

Prof. HAROLD B. DIXON, M.A., F.R.S., President,
in the Chair.

It was announced that the Council had appointed the following Committees for 1909-1910:—

Finance Committee—Messrs. E. G. Hooper, G. T. Moody, T. E. Thorpe, W. A. Tilden, and the Officers.

House Committee—Messrs. W. R. Dunstan, J. E. Reynolds, W. J. Russell, J. M. Thomson, T. E. Thorpe, W. A. Tilden, and the Officers.

Library Committee—Messrs. E. C. C. Baly, F. D. Chattaway, B. Dyer, W. Gowland, A. Harden, C. A. Keane, A. Lapworth, E. J. Mills, J. M. Thomson (Chairman), J. A. Voelcker, J. Wade, the Editor, and the Officers.

Publication Committee—Messrs. W. R. Dunstan, C. E. Groves, J. T. Hewitt, A. McKenzie, R. Meldola, G. T. Morgan, T. E. Thorpe, and the Officers.

Research Fund Committee—Messrs. G. T. Beilby, J. N. Collie, A. D. Hall, A. Liversidge, R. Meldola, R. Messel, Sir A. Pedler, W. H. Perkin, J. E. Reynolds, W. A. Tilden, and the Officers.

Certificates were read for the first time in favour of Messrs. John Harbord Edge, Great Marle, Smithills, Bolton; Harold Hibbert, M.Sc., Ph.D., Creston, Marple Bridge, Derbyshire; Roland Josiah May, Granaugh Villa, Dunbar, N.B.; Thomas Napier, Arbiene, Clarkston, Busby.

Of the following papers, those marked * were read:—

*97. "The Affinity Values of certain Alkaloids." By VICTOR HERBERT VELEY.

Determinations have been made of the affinity value of some of the more important alkaloids by the methyl-orange and borax precipitation methods, the latter only being put forward as giving approximate results in cases in which the electric conductivity and ester catalysis methods cannot be applied.

It was shown that the affinity values of only a few alkaloids are less than $1 \cdot 10^{-7}$, those of the greater number

are between the limits of $1 \cdot 10^{-7}$ and $3 \cdot 10^{-5}$ (value of ammonia), and lastly, only a few have a value higher than the last figure, and hence may be classed with the tetra-alkylammonium hydroxides.

It appears that when alkaloids consist of two conjoint residues which, if considered each by itself, would give affinity values of a widely different order, such as piperidine or benzylamine on the one hand, and quinoline or pyrrolidine on the other, the stronger residue is modified by the presence of the weaker. It seems to be immaterial whether each residue contains a nitrogen atom, and whether such an atom is common to both.

The affinity values determined by the methods applied, and collected together for the sake of comparison, illustrate the difficulty of obtaining salts, B_2HCl , in the case of certain dinitrogen alkaloids.

DISCUSSION.

Prof. KIPPING understood that the author's method was based on the first appearance of a permanent precipitate of the alkaloid; but as some alkaloids were soluble in solutions of some salts, a fact which was often observed in dealing with compounds containing silicon, he asked if the formation of a precipitate indicated corresponding conditions in all cases?

Dr. LESSING asked the author if he had found any marked difference in affinity values of tropine derivatives with the nitrogen in the α - and δ -positions respectively to the carboxyl group. Willstätter and he found some years ago that with regard to exhaustive methylation, pyrrolidine- and piperidine-carboxylic acids may be classified into two groups, namely, those of the ecgonine type, corresponding with β -amino-acids, in which methylation effects the disruption of the ring, and those of the α -ecgonine type corresponding with α -amino-acids, which resist all attempts to open up the ring.

Dr. VELEY replied that the point of initial precipitation of the alkaloid by the hydrolysed borax solution was perfectly sharp in all cases examined with the single exception of papaverine; the precipitate initially formed re-dissolved at first quickly, and subsequently more slowly. The method proposed could only be applied for alkaloids the solubility of which in water was of the order 1 : 1000.

The affinity values of tropine and its derivatives had been dealt with in a previous communication.

There appeared to be a certain confusion in the minds of certain writers between basicity and affinity values; although there was, doubtless, some correlation between these two factors, yet in the present state of our knowledge it appeared prudent to keep them quite distinct from one another.

*98. "*Phycoerythrin, the Pigment of the Red Alga.*" By EDWARD KENNETH HANSON.

Phycoerythrin has been investigated as to (1) its action with regard to light, and (2) its chemical nature. With respect to the first point, Schütt (*Ber. Deut. Bot. Ges.*, 1888, vi., 307) has shown that phycoerythrin absorbs bluish green light and gives an orange fluorescence. The author has confirmed this observation, and has further photographed the fluorescence spectrum, thus succeeding in demonstrating that the fluorescent light gives two bands coincident with two of the absorption bands of chlorophyll. This is in harmony with the hypothesis that phycoerythrin assists assimilation in deep-water plants by absorbing the light available at these depths, and degrading it to yellow and red light which can be utilised by the chlorophyll.

With regard to the chemical nature of phycoerythrin, the evidence is very inconclusive, owing to the impossibility (up to the present) of obtaining pure phycoerythrin. Molisch (*Bot. Zeit.*, 1894, p. 177) has suggested that the pigment is protein; but it does not give the biuret reaction, and its nitrogen content is too low (not much greater than 6 per cent) for a true protein. It is, however, a colloid, soluble only in water, and precipitated by the ordinary protein precipitants, and appears to be related to proteins, as it yields leucine on hydrolysis with acids. It is attacked by trypsin, but not by pepsin.

DISCUSSION.

Mr. CHASTON CHAPMAN said it had occurred to him that the colouring matter of certain red torulae which he was examining, and which appeared to be very closely allied to carotene, might conceivably be of some assistance to the organism in protecting the protoplasm from the injurious effects of the violet rays of light. He had made experiments on this point, and had found that these organisms, unlike many of the yeasts, grew equally well whether exposed to red or violet rays. He did not see, however, that in the case of the alga referred to by the author, any such protective effect could come into play.

Dr. FEILMANN suggested that dyeing experiments on the material might throw some light on the chemical nature and composition of the colouring principle; it might, for instance, be possible in this way to discover whether the substance contained nitrogen, by dyeing on to cotton and then testing for that element.

The PRESIDENT asked how the author was sure that algin was not precipitated with the colouring matter.

In reply, Mr. HANSON said that no experiments had been made in dyeing. The solution of phycoerythrin in pure water deteriorated very rapidly, but the presence of a small amount of eucalyptus oil or other antiseptic enabled solutions to be kept, even if exposed to light, for months. In answer to the President's questions, he did not consider that separation from algin was complete; that was, indeed, the chief difficulty in attempting to study the chemical nature of phycoerythrin. Boiling with sodium carbonate decolorised the solution. With regard to Dr. Cain's suggestion, the solid material had not been tested for bromine or iodine, and although it gave a qualitative reaction for sulphur, an amount sufficient for quantitative estimation had not been found.

*99. "*isoAmygdalin and the Resolution of its Hepta-acetyl Derivative.*" By FRANK TUTIN.

Since isoamygdalin crystallises only with difficulty, and melts indefinitely at relatively so low a temperature ($125-140^\circ$), the author considers that it does not consist of a definite, partially racemic compound, but is merely a mixture of amygdalin and the corresponding derivative of *d*-mandelonitrile. Moreover, it appears that the latter derivative predominates, since the mandelic acid yielded by isoamygdalin is slightly dextrorotatory.

As isoamygdalin itself cannot be fractionally crystallised in a satisfactory manner, its acetyl derivative has been employed. This has been separated into its components, namely, hepta-acetylamygdalin and the hepta-acetyl derivative of the unknown stereoisomeride of amygdalin. Hepta-acetylneoamygdalin, $C_{34}H_{41}O_{18}N$, crystallises in long needles, melts at 174° , and has $[\alpha]_D^{20} = -65.6^\circ$ in chloroform. On hydrolysis with concentrated hydrochloric acid, it yields *d*-mandelic acid.

*100. "*The Stability of Compounds Derived from Tertiary Amines and Magnesium Alkyl Halides.*" By HAROLD HIBBERT.

A determination of the chemical "affinity" of diethylaniline for magnesium methyl iodide by the method previously described by the author (*Proc. Chem. Soc.*, xxv., 57) shows a very low value relative to that of monoethylaniline. This is in agreement with the observation of Tschelinzeff (*Ber.*, 1907, xl., 1495) that the heat of combination of diethylaniline with magnesium propyl iodide is very small. It follows from these two facts that the quaternary compound, $NEt_2Ph.MgMeI$, must be relatively very unstable. The author has been able to show that this instability is a general property of the compounds derived from tertiary amines, decomposition into free base and magnesium alkyl halide occurring at $200-280^\circ$. This is true of the derivatives from triethylamine, tripropylamine, diethylaniline, and dimethylaniline; pyridine forms an exception. The original amine is obtained whether magnesium ethyl bromide or magnesium methyl iodide is employed, and this point is being investigated with a large number of alkyl halides.

*101. "A New Method for the Separation of Tertiary from Secondary and Primary Amines." By HAROLD HIBBERT and ARCHIBALD WISE.

The relative instability of the derivatives from tertiary amines and magnesium alkyl halides (see preceding note) led the authors to investigate the stability of the compounds derived from the action of magnesium alkyl halides on secondary and primary amines. It has been found that the derivatives R_2NMgI and $RNHMgI$ respectively are very stable substances, only decomposing when strongly heated, whereas the derivatives with tertiary amines decompose between 200° and 280° . Based on these facts the following simple method has been devised for the separation of tertiary amines from mixtures with secondary and primary amines:—To the mixture of amines (either alone or in ethereal solution) is added a quantity of an ethereal solution of magnesium ethyl bromide sufficient to combine with the whole of the secondary (or primary, respectively) amine, together with 20 to 30 per cent of the theoretical amount required for the tertiary amine (this amount is sufficient on account of the very great difference in their chemical "effnergies" for the Grignard reagent), and the product then distilled from an oil-bath. Ether distils over at first, followed as the temperature in the oil-bath rises to 200 – 280° by the pure tertiary amine. The last traces are swept out by dry hydrogen or other indifferent gas. The secondary (or primary, respectively) amine is recovered by adding water and distilling in a current of steam. Even when using very small quantities (for example, 5 to 10 grms.) it is possible to recover 70 to 80 per cent of the products in this way, and the tertiary amine is obtained quite free from secondary or primary amine. The method has been applied to the separation of the following mixtures:—Di- and tri-ethylamine, di- and tri-propylamine, mono- and di-methylaniline, mono- and di-ethylaniline, aniline and dimethylaniline.

102. "The Preparation and Properties of the N-Tribromo-substituted Hydrazines (the Diazonium Perbromides)." By FREDERICK DANIEL CHATTAWAY.

The preparation of the N-tribromophenylhydrazines from the hydrazines by substitution was described.

All the N-tribromohydrazines when brought into contact with free bromine combine with it and form compounds only stable under a considerable pressure of bromine vapour, in which the halogen is much less firmly attached than when replacing hydrogen combined with tervalent nitrogen.

In the preparation of the N-tribromohydrazines from diazonium salts, if liquid bromine is used, these unstable compounds are formed locally, and have to be removed from the solid substituted hydrazines by washing with ether or exposure to the air. They are also formed when the N-tribromohydrazines are placed in water, these compounds being in part dissociated into diazonium salts and free bromine, the halogen set free combining to a considerable extent with the remainder of the N-substituted hydrazines, and forming with them a more or less pasty mass.

The behaviour of a number of N-tribromohydrazines when heated, when exposed to dry and moist air, when suspended in water or concentrated hydrochloric acid, and when dissolved in alcohol or acetic acid, was also described.

103. "The Coloured Salts and Derivatives of the Thiovioluric Acid Group." (Preliminary Note). By PERCY CLAUDE CAMERON ISHERWOOD.

In view of the interesting colour relations of the salts of the violuric acid group, the author is studying the influence of the replacement of oxygen by sulphur in this acid and some of its derivatives.

Thiovioluric Acid, $CS<\begin{smallmatrix} NH\cdot CO \\ NH\cdot CO \end{smallmatrix}>C:N\cdot OH$.—The mono-sodium salt of this acid has been prepared by the action of acetic acid on equivalent quantities of sodium thiobarbiturate and sodium nitrite in aqueous solution below 0° . From this the free acid was obtained in small yellow

needles by the action of cold dilute hydrochloric acid. Its aqueous solution has the characteristic violet colour. The following salts have been prepared, and exhibit a wide range of colours:—Lithium, sodium, potassium, ammonium, calcium, strontium, barium, magnesium, mercuric, lead, silver, and cadmium.

1 : 3-Diphenylthiobarbituric Acid, $CS<\begin{smallmatrix} NPh\cdot CO \\ NPh\cdot CO \end{smallmatrix}>CH_2$.

—This was prepared by heating together 5-diphenylthiocarbamide, phosphoryl chloride, and malonic acid (compare Miss Whiteley, *Trans.*, 1907, xci., 1330); it crystallises from alcohol in bulky pale yellow needles.

1 : 3-Diphenylthiovioluric Acid, $CS<\begin{smallmatrix} NPh\cdot CO \\ NPh\cdot CO \end{smallmatrix}>C:N\cdot OH$.

—1 : 3-Diphenylthiobarbituric acid was dissolved in dilute ammonia, and treated successively with equivalent quantities of sodium nitrite and acetic acid. A reddish precipitate of the above acid was formed. The work is being extended to other derivatives of thiovioluric acid, especially with a view to the examination of the colour and absorption spectra of solutions of salts.

104. "Studies in the Barbituric Acid Series. Part II. 1 : 3-Diphenyl-2-thiobarbituric Acid and some Coloured Derivatives." By MARTHA ANNIE WHITELEY and the late HAROLD MOUNTAIN.

In a recent paper by Hantzsch, "Über Pantochromie und Chromoisomerie von Violuraten und verwandten Oximidoketon-Salzen" (*Ber.*, 1909, xlii., 966), two references are made to work that is being conducted by R. Robison on diphenylvioluric acid; as this compound, the first of the aryl-substituted violuric acids, and a large number of its salts and derivatives were prepared by one of the authors (Whiteley, *Trans.*, 1907, xci., 1330), and the work is still being continued, it was deemed advisable to describe further results obtained in this series.

1 : 3-Diphenyl-2-thiobarbituric acid, $CS<\begin{smallmatrix} NPh\cdot CO \\ NPh\cdot CO \end{smallmatrix}>CH_2$,

m. p. 244° , forms pale yellow needles, and condenses with aldehydes and ketones to yield compounds of the type $CS<\begin{smallmatrix} NPh\cdot CO \\ NPh\cdot CO \end{smallmatrix}>C:R$, which are reduced to the corre-

sponding saturated derivative, $CS<\begin{smallmatrix} NPh\cdot CO \\ NPh\cdot CO \end{smallmatrix}>CH\cdot HR$;

5-isopropenyl-1 : 3-diphenyl-2-thiobarbituric acid, $CS<\begin{smallmatrix} NPh\cdot CO \\ NPh\cdot CO \end{smallmatrix}>C:CM_e2$, m. p. 260 – 262° , forms canary-

yellow prisms; 5-isopropyl-1 : 3-diphenyl-2-thiobarbituric acid, m. p. 237 – 240° , is pale yellow; 5-benzylidene-1 : 3-

diphenyl-2-thiobarbituric acid, $CS<\begin{smallmatrix} NPh\cdot CO \\ NPh\cdot CO \end{smallmatrix}>C:CHPh$,

m. p. 254° , forms orange-yellow prisms; 5-benzyl-1 : 3-diphenyl-2-thiobarbituric acid, $CS<\begin{smallmatrix} NPh\cdot CO \\ NPh\cdot CO \end{smallmatrix}>CH\cdot CH_2Ph$,

m. p. 187° , forms pale yellow needles; 5-o-nitro-

benzylidene-1 : 3-diphenyl-2-thiobarbituric acid, $CS<\begin{smallmatrix} NPh\cdot CO \\ NPh\cdot CO \end{smallmatrix}>C:CH\cdot C_6H_4\cdot NO_2$, m. p. 236° , forms dull

orange needles, and 5-cinnamylidene-1 : 3-diphenyl-2-

thiobarbituric acid, $CS<\begin{smallmatrix} NPh\cdot CO \\ NPh\cdot CO \end{smallmatrix}>C:CH\cdot CH:CHPh$,

m. p. 278° , forms brilliant crimson prismatic needles.

1 : 3-Diphenyl-2-thiobarbituric acid and its 5-aryl-substituted derivatives condense with aromatic diazonium chlorides to form the corresponding hydrazone or azo-

derivative:—1 : 3-Diphenyl-2-thioalloxanphenylhydrazone, $CS<\begin{smallmatrix} NPh\cdot CO \\ NPh\cdot CO \end{smallmatrix}>C:N\cdot NHPh$, m. p. 291° , forms

brilliant orange prismatic needles; 1 : 3-diphenyl-2-thioalloxan-p-nitrophenylhydrazone, $CS<\begin{smallmatrix} NPh\cdot CO \\ NPh\cdot CO \end{smallmatrix}>C:N\cdot NH\cdot C_6H_4\cdot NO_2$, m. p. 288° , crystal-

lises in orange-red needles, and 5-benzeneazo-

1 : 3-diphenyl-5-benzyl-2-thiobarbituric acid, $CS<\begin{smallmatrix} NPh\cdot CO \\ NPh\cdot CO \end{smallmatrix}>C<\begin{smallmatrix} CH_2Ph \\ N:NPh \end{smallmatrix}>$, m. p. 135° , crystallises in

yellow needles.

Two isomeric varieties of 1:3-diphenyl-2-thiovioluric acid have been obtained differing in colour and melting-point, and a similar isomerism has been observed among the pyridine, piperidine, and alkali salts of the acid. α -1:3-

Diphenyl-2-thiovioluric acid, $\text{CS} \begin{smallmatrix} \text{NPh} \cdot \text{CO} \\ \text{NPh} \cdot \text{CO} \end{smallmatrix} \text{C} : \text{N} \cdot \text{OH}$ m. p. 211—212°, obtained by the action of ethyl nitrite on 1:3-diphenyl-2-thiobarbituric acid, forms deep red prismatic needles, and a bluish violet hydrated acid,

$\text{CS} \begin{smallmatrix} \text{NPh} \cdot \text{CO} \\ \text{NPh} \cdot \text{CO} \end{smallmatrix} \text{C} : \text{N} \cdot \text{OH} \cdot \text{H}_2\text{O}$, is obtained by the action of sodium nitrite and hydrochloric acid on the barbituric acid; β -1:3-diphenyl-2-thiovioluric acid (probably,

$\text{CS} \begin{smallmatrix} \text{NPh} \cdot \text{CO} & & \text{NH} \\ & \diagdown & / \\ & \text{C} & \\ & / & \diagdown \\ \text{NPh} \cdot \text{CO} & & \text{O} \end{smallmatrix}$, m. p. 224°, is obtained as a

yellowish brown crystalline powder when the pyridine salt is heated at 100° or boiled with alcohol. The *piperidine* salt, $\text{C}_{16}\text{H}_{11}\text{O}_3\text{N}_3\text{S} \cdot \text{C}_5\text{NH}_{11}$, exists in two crystalline forms, one grey, m. p. 181—182°, and one pale red, m. p. 187°; the two varieties of the *pyridine* salt $\text{C}_{16}\text{H}_{11}\text{O}_3\text{N}_3\text{S} \cdot \text{CNH}_5$, are green and dull red respectively. The *potassium* salt, $\text{C}_{16}\text{H}_{10}\text{O}_3\text{N}_3\text{SK}$, is obtained in dark olive-green cubic crystals by the action of potassium hydroxide on the α -violuric acid; the *sodium* salt, $\text{C}_{16}\text{H}_{10}\text{O}_3\text{N}_3\text{Na}$, is similarly obtained in rose-red needles; when, however, an alcoholic solution of 1:3-diphenyl-2-thiobarbituric acid is added to an aqueous solution of potassium or sodium nitrite, the potassium or sodium salt of 1:3-diphenyl-2-thiovioluric acid is obtained as a violet or purple microcrystalline powder respectively. The *ferrous* salt, $(\text{C}_{16}\text{H}_{10}\text{O}_3\text{N}_3\text{S})_2\text{Fe}$, is a deep blue crystalline powder with a purple reflex.

The melting-points recorded in this preliminary communication are in all cases temperatures of decomposition, and therefore vary with rate of heating.

105. "Nitrosoacetyl-amino-derivatives of the Benzene and Diphenyl Series." By JOHN CANNELL CAIN.

In continuation of previous work (*Trans.*, 1908, xciii., 681), the author has prepared the following compounds:—2-Nitrosoaceto-p-toluidide, $\text{NO} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NHAc}$, pale yellowish brown crystals, m. p. 195°; 6-nitroso-m-toluidide, green needles, m. p. 128—129°; 5-nitrosoaceto-o-toluidide, green needles, m. p. 135—136°; 2-chloro-4-aminoacetanilide, $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{NHAc}$, pale yellow plates, m. p. 111°; 2-chloro-4-nitrosoacetanilide, green needles, m. p. 112—113°; and 3:3'-dichloro-4:4'-diacetyldiaminoazobenzene, $\text{NHAc} \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{NHAc}$, pale yellow needles, m. p. 280°.

The monoacetyldiamines of the diphenyl series can readily be prepared by the action of acetic anhydride on an aqueous alcoholic solution of the corresponding base. Monoacetylitolidine, $\text{NHAc} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NH}_2 \cdot \text{H}_2\text{O}$, forms white shining plates, m. p. 103°, and on oxidation with Caro's acid yields 4-nitroso-4'-acetylamino-3:3'-ditolyl, $\text{NO} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NHAc}$, pale brown crusts, m. p. 154—155°. Monoacetylbenzidine on similar treatment furnishes 4-nitroso-4'-acetylamino-diphenyl, $\text{NO} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NHAc}$, yellowish brown feathery needles, m. p. about 275°.

106. "The Rate of Reaction of the Triphenylmethane Dyes with Acid and Alkali. Part II. Brilliant Green and Malachite Green." By NEVIL VINCENT SIDGWICK and TOM SIDNEY MOORE.

In a previous paper (*Zeit. Physik. Chem.*, 1907, lviii., 385) the authors have investigated the rate of reaction of brilliant green (the salt of tetraethyldiaminotriphenylcarbinol) with alkali and with hydrochloric acid. They have now examined the action of nitric acid on this dye, and that of nitric and hydrochloric acids, and of alkali on the corresponding tetramethyl compound, malachite green. The method adopted in all cases was to determine the concentration of the dye by measuring the colour of the solution in a Donnan tintometer.

The behaviour of the two dyes was found to be very similar, and also that of the two acids.

1. The velocity of formation of the carbinol in presence of alkali is proportional to the product of the concentrations of the dye and the alkali, and is found to be more than twice as great as that deduced for much higher concentrations by Gerlinger (*Ber.*, 1904, xxxvii., 3958) from the conductivity measurements of Hantzsch and Osswald (*Ber.*, 1900, xxxiii., 278). This is probably due to the dye-base not being wholly ionised, and would be accounted for by a dissociation constant of 0.00531, about four times that of diethylamine.

2. Acids act on the dye-salt to form a colourless acid salt, and at equilibrium $k_1 \times \text{C}_{\text{dye-salt}} \times \text{C}_{\text{acid}} = k_2 \times \text{C}_{\text{acid salt}}$, where k_1/k_2 is independent of the strength of the acid, but k_1 and k_2 vary inversely as the cube root of the concentration of the acid.

3. When a solution of the carbinol is treated with acid, it first yields the dye-salt, which is then converted reversibly into the acid salt. The velocity of this last reaction being known, that of the first can be determined. A graphic method, due to Mr. H. G. J. Mosely, was described, by which the velocity can be calculated from the somewhat complicated expression obtained, which does not admit of direct solution. The velocity is proportional to the concentration of the carbinol and to the two-thirds power of that of the acid.

The various constants obtained for the two dyes and for the two acids show a very close agreement, the difference never amounting to 25 per cent, and in most cases being much smaller.

107. "The Rate of Reaction of the Triphenylmethane Dyes with Acid and Alkali. Part III. Diaminotriphenylcarbinol." By NEVIL VINCENT SIDGWICK and ALBERT CHERBURY DAVID RIVETT.

The velocity of reaction of this unsubstituted dye was determined by the same method. The general results are similar, but the constants are all larger, and certain modifications are introduced by the fact that this dye is a much weaker base.

1. With alkali the reaction is unimolecular as before, but the constant increases much more slowly than the alkali, owing no doubt to the dye-base being largely undissociated. The observed results agree with those calculated for a dissociation constant of 0.0004 (about 1/12 of that of brilliant green) when the alkali is not too weak. They indicate that if the carbinol is formed from the non-ionised portion of the dye-base, this dye reacts 1.6 times as fast as brilliant green, but if from the ions, 21 times as fast. The former view is therefore more probable.

2. If a solution of the dye is treated with a small quantity of acid, its colour increases, owing to the disappearance of hydrolysis, whilst a further addition of acid diminishes the colour, from the formation of the acid salt. In N/125,000-solution the dye is hydrolysed to the extent of 33.5 per cent, giving the dissociation constant of the base as 7.5×10^{-9} . This obviously refers to the system (carbinol $\rightleftharpoons$ dye-base) at equilibrium, and is 50,000 times less than the constant of the dye-base itself. This is an instance of the true "abnormal hydrolysis" of a pseudo-base.

The constants k_1 and k_2 of the formation and dissociation of the acid salt (see preceding paper) vary inversely as the square root (instead of the cube root) of the concentration of the acid.

3. The action of acid on the carbinol is the same as in the previous cases, the unimolecular constant M being proportional to the two-thirds power of the strength of the acid.

The values of these constants (compared by reference to a normal acid) are in all cases higher for this dye than for the alkylated derivatives, brilliant green and malachite green, k_1 being about 7 times, k_2 1.5 times, and M 3 times as great.

108. "Indican." (Part II.). By ARTHUR GEORGE PERKIN and FREDERICK THOMAS.

p-Nitrobenzaldehydeindogenide, $\text{C}_{15}\text{H}_{10}\text{O}_3\text{N}_2$ (Baeyer,

Ber., 1881, xiv., 1745). is readily formed by hydrolysing indican with acid in the presence of *p*-nitrobenzaldehyde, and the reaction may be employed for the quantitative estimation of the glucoside. In this respect piperonal is not so serviceable, and the yield of methylenedioxybenzaldehydeindogenide, $C_{16}H_{11}O_3N$, orange needles, m. p. 223–224°, by the process employed was but 96 per cent. Dihydroxybenzaldehydeindogenide, $C_{15}H_{11}O_3N$, from indican, acid, and protocatechualdehyde, orange-red needles, m. p. 264–265°, soluble in strong alkali with a blue colour, and dyeing mordanted fabrics, is more difficult to isolate, owing to the formation of brown secondary products. The acetyl derivative, $C_{15}H_9O_3N(C_2H_3O)_2$, orange needles, melts at 182°. Hydroxybenzaldehydeindogenide, from *p*-hydroxybenzaldehyde, $C_{15}H_{11}O_3N$, orange-red needles, m. p. 267–269°, soluble in alkali with a red coloration, gives the acetyl compound, $C_{15}H_{10}O_2N, C_2H_3O$, orange leaflets, m. p. 223–224°, and is not a dye stuff. The *p*-nitro- and methylenedioxy benzaldehydeindogenides can easily be prepared in quantity by employing the leaf extracts of *I. sumatrana* and *I. arrecta* in the place of pure indican.

When indican is hydrolysed by sulphuric acid (4 cc. in 1000 cc. of water) at 60°, simultaneously oxidising with air, the yield of colouring matter is but 85 per cent, due in part to the formation of brown secondary products. The latter reaction does not so readily occur when the equivalent quantity of hydrochloric acid is employed, and the yield of colouring matter (about 93·5 per cent) is thus higher. In addition to indigotin, indirubin is also formed in some quantity under these conditions. Stronger solutions of sulphuric and hydrochloric acids at the boiling-point in absence of air give respectively with indican identical brown products insoluble in alkali, from which, in addition to the indoxyl brown previously described (*Trans.* 1907, xci., 1715), an analogous substance more sparingly soluble in alcohol (found, $N = 9\cdot65$) was isolated.

The action of acid in the cold for a longer period (compare Schunck and Roemer, *Ber.*, 1879, xii., 2311) has a similar effect, and indoxyl brown is thus formed. The brown product obtained from the leaf extracts of the *Indigoferae* by means of acid differs from indoxyl brown in that it is soluble in alkali, and appears to arise from a condensation of indoxyl with other compounds derived from the plant. In view of recent discussion on the melting-point of dextrososazone (Tutin, *Proc.*, 1907, xxiii., 250), the pure sugar derived from indican was converted into its acetyl derivative, and this was identical with acetyldextrose.

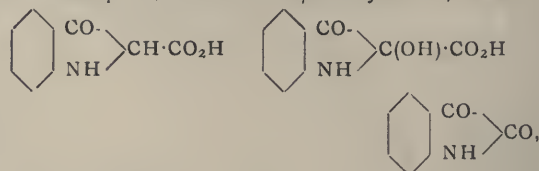
109. "*Indican*." (Part III.). By FREDERICK THOMAS, WILLIAM POPPLEWELL BLOXAM and ARTHUR GEORGE PERKIN.

The authors have carried out experiments on the hydrolysis of pure indican by means of indimulsine, its specific enzyme (Beyerinck, *Proc. K. Akad. Wetensch. Amsterdam*, 1899, i., 120; Hazewinkel, *Ibid.*, 1900, ii., 512; and van Romburgh, *Ibid.*, 1899, ii., 344), and on the air oxidation of the solutions of indoxyl thus produced under a variety of conditions. The results indicate that, owing to the unstable nature of indoxyl, changes occur both during the fermentation and oxidation processes which prevent these reactions from proceeding in a quantitative manner. The best yields of colouring matter were given when a small amount of acid was present during the fermentation (compare Beyerinck, *loc. cit.*), and the fermented liquid was then oxidised in the presence of a trace of ammonia.

110. "*Indoxylic Acid*." By ARTHUR GEORGE PERKIN. The examination of a sample originally consisting of commercial indoxylic acid, which had remained unopened for some years, showed that no indoxyl or indoxylic acid was now present. The product contained:—

Matter soluble in alkali		32·94 per cent
Indirubin		42·37 "
Indigotin		17·30 "
Moisture		2·15 "
Ash		1·05 "
Insoluble in nitrobenzene by difference		4·19 "

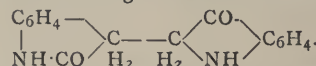
The oxidation involved appears to have arisen from the gradual admission of air, and whereas the formation of indigotin is easily accounted for, it is considered that the predominance of indirubin has arisen from the formation, in the first place, of isatin from ψ -indoxylic acid, thus—



and its subsequent condensation with indoxyl. That portion of the matter soluble in alkali contained isatin and an acid resembling phenylglycine-*o*-carboxylic acid, but the main bulk consisted of an amorphous brown product, from which was isolated a brown substance very closely resembling and possibly identical with the chief constituent of the indigo-brown (*Trans.*, 1907, xci., 279) which is present in natural indigo. The examination of two other products derived in the same manner from indoxylic acid gave results of a similar character, and it thus appears likely that in these circumstances the changes involved are of a normal character.

111. "*The Reduction of Indirubin*." By ARTHUR GEORGE PERKIN.

It has been shown by Fasal (*Mitt. K. Tech. Gew.-mus. Wien.*, 1895, 307) that when indirubin is reduced by zinc dust and alkali under conditions of indigo-vat practice, the indirubin-white at first formed soon undergoes further reduction, indoxyl being thus produced, and this in the dyeing operation is converted into indigotin. A study of the reaction with a large quantity of indirubin derived from an extract of *I. sumatrana* by means of isatin has shown that under these conditions oxindole is also produced, and this, obtained in colourless needles, m. p. 120°, was identified by means of its nitroso-compound, m. p. 204–206°, and by oxidation with ferric chloride to isatin. The formation of indoxyl and oxindole is readily understood by reference to the following scheme:—



and the behaviour of indirubin in this respect does not suggest that its presence in natural indigo can be economically advantageous. In addition to oxindole, a small quantity of a yellow basic substance resembling the di-indole of Schutzenberger (*Fabresb.*, 1877, 511), $C_{16}H_{14}N_2$, was also formed in this reaction. A quantitative study of the reduction of indirubin by this method is in progress.

112. "*Solubility of Lead Sulphate in Concentrated Solutions of Sodium and Potassium Acetate*." By JOHN JACOB FOX.

The increased solubility of lead sulphate in concentrated solutions of sodium and potassium acetates is due to the formation of lead acetate in solution, conclusive evidence being obtained from the examination of the system potassium acetate-lead sulphate. In this case no sulphate was dissolved, although as much as 19 per cent of lead acetate was found in one of the solutions. As regards the system sodium acetate-lead sulphate, the proportion of sulphate in solution was equivalent to the lead dissolved.

The solid phase in the potassium acetate system was altered, lead potassium sulphate, $PbK_2(SO_4)_2$, being formed, but no corresponding double salt was obtained from the sodium acetate system. The absence of double salt in the latter case probably arises from the fact that the amount of sodium sulphate formed from the lead sulphate by sodium acetate is insufficient, considered alone, to saturate the solution at 25°. The solubility curve for sodium sulphate in sodium acetate solution is entirely different in character from that of potassium sulphate in potassium acetate, the solubility in the latter case decreasing rapidly with increasing concentration of the potassium acetate.

Although the solubility of lead sulphate is shown to be due to the formation of lead acetate in solution, the solubility curves do not coincide with those derived from the system lead acetate-alkali acetate, since the presence of sulphates in the solid phases, tends to reduce the solubility of the lead.

113, "The Colour and Constitution of the Alkyl Iodides of Cyclic Bases." By CHARLES KENNETH TINKLER.

From an examination of the absorption spectra of the methiodides of cyclic bases, it is suggested that the colour of the alkyl iodides is due to polymerisation, the linking taking place between the iodine atoms.

A similar view was recently put forward by Hantzsch (*Ber.*, 1909. xlii., 68). The results of molecular-weight determinations in support of this view were communicated to Dr. Decker by the author in November, 1907, but were not published.

Phenylacridine methiodide in chloroform is termolecular, and the solution, like the solid substance, is strongly coloured (compare Hantzsch, *loc. cit.*).

Molecular-weight determinations carried out in diphenylamine solution by the cryoscopic method also indicate that the substances when coloured are polymerised. It was pointed out that the alkyl iodides of piperidine and tetrahydroquinoline derivatives are colourless.

114, "A Method for Investigating Dissociation Equilibria in Solutions, and its Application to the Study of Aqueous Potassium Mercuriodide Solutions." By HARRY MEDFORTH DAWSON.

A method for the investigation of dissociation equilibria in solutions was described. The type of equilibrium in question may be represented by the reversible equation $A + mB \rightleftharpoons AB_m$, according to which one mol. of the substance unites with m mols. of B to form the dissociating complex compound AB_m .

The method consists in adding to the solution of A and B a third substance C, which also combines with A to form a dissociating compound AC_n , the dissociation constant of which is known. If the concentration of uncombined C in the solution is determined, that of the compound AC_n follows at once, and by combining these data with the dissociation constant of the compound AC_n , the concentration of uncombined A in the solution can be obtained. Under certain conditions this leads at once to a knowledge of the molar ratio of A to B in the compound AB_m .

The method has been applied to the examination of solutions of mercuric iodide in potassium iodide. The experimental results show that the amount of potassium iodide which is combined with a given quantity of mercuric iodide diminishes as the relative concentration of the mercuric iodide in the solution increases. In solutions which contain relatively little mercuric iodide, the compound $2KI, HgI_2$ is the chief complex constituent; on the other hand, solutions which are nearly saturated with mercuric iodide contain the complex compound $3KI, 2HgI_2$ as the chief constituent.

PHYSICAL SOCIETY.

Ordinary Meeting, April 23rd, 1909.

Dr. C. CHREE, F.R.S., President, in the Chair.

A PAPER by Prof. W. H. BRAGG and Mr. J. L. GLASSON, "On a want of Symmetry shown by Secondary X-rays," was read by Prof. Bragg.

When a primary X-ray strikes an atom, a secondary X-ray sometimes start out from the place of impact. The experiments described in the paper were made with the object of comparing the intensity of emission of the secondary X-ray in a direction making an angle of about 45° with the primary with the intensity in a direction making an angle of 135° , and therefore turning back almost completely. It was found that in the case of atoms of platinum, tin, or aluminium, or of such light atoms as are

contained in celluloid, the former was larger than the latter, being sometimes three times as great. Madsen has obtained similar but much greater inequalities in the case of the γ -rays. When atoms of copper or iron were tested, atoms which give rise to a very soft radiation, there was little inequality. A similar inequality effect also occurs in the case of β -rays. On the original pulse theory, calculation showed that there should be no inequality of the secondary X radiation in any case. If that theory were abandoned, as most writers now agreed to do, and the X-rays were supposed to be bundles of energy travelling through space, there did not appear to be sufficient definition of such entities as would enable any comparison to be made between theory and experiment. If the rays were supposed to be material, the facts were generally in agreement with expectation, and afforded another instance of close parallelism between the phenomena of the X and the γ -rays.

Prof. C. H. LEES said that Prof. Bragg had given a lucid account of his theories of γ and X-rays. His researches would make physicists more careful in accepting the æther-pulse theory. He asked if it was likely that better means would be devised to discriminate between various forms of γ and X-rays than dividing them into "hard" and "soft" radiations. He thought many discrepancies could be attributed to this want of discrimination.

Mr. C. A. SADLER pointed out that, whatever lack of symmetry might exist in the emergence and incidence secondary X radiations from a plate of a substance which was a source of scattered primary radiations, Prof. Bragg's results conclusively proved that such lack of symmetry did not exist when the plate was a source of homogeneous radiation. If then it was a necessary condition of Prof. Bragg's theory that such lack of symmetry should exist with secondary X radiations, we must either conclude that the theory here breaks down or that these homogeneous radiations are not X radiations as usually understood. It was to be noted also that the measured lack of symmetry (ignoring the lack of symmetry in the case of homogeneous beams, which had been shown to be only apparent) in the most pronounced cases was small compared with those obtained with γ -rays.

Prof. BRAGG, referring to the remarks of Prof. LEES, said that for precision the actual speed of all electrons ought to be measured. Instead of measuring the speed the penetrating power might be determined.

A paper entitled "Transformations of X-rays" was read by Mr. C. A. SADLER.

It has been shown that the members of the group of metals Chromium—Silver emit under suitable primary beams radiations which are homogeneous and which increase in penetrating power with increase of atomic weight of the radiator. Using these homogeneous beams, the tertiary radiation excited by them in other metals has been studied by the author. It was found that the tertiary radiation excited in any member of the group Cr—Ag was homogeneous, and its penetrating power was that characteristic of the radiation from the substance when excited by a primary beam. With any given tertiary radiator it was found that the intensity of the homogeneous type of radiation emitted when the homogeneous radiations from the members of the group Cr—Ag successively fell upon the radiator was inappreciable unless the exciting radiation was more penetrating than that characteristic of the radiator. Defining a quantity k such that the fraction of the energy of the secondary beam passing normally through a thin layer δx of the tertiary radiator which was transformed in tertiary radiation $= k\delta x$, it was found that as long as the penetrating power of the secondary beam was less than that characteristic of the tertiary radiator, k was sensibly zero. When the secondary beam became more penetrating than that characteristic of the tertiary radiator, k increased rapidly to a maximum and then decreased over a considerable range, with increase of penetrating power

of the secondary, as a linear function of the ionisation produced in a thin layer of air by the secondary beam. It has been shown that when the characteristic radiation is excited in a substance, a corresponding increase in the absorption of the exciting radiation by that substance takes place. If λ' denote the increase in the value of the absorption coefficient of the exciting beam by the material of the tertiary radiator consequent upon the emission of the tertiary radiation, k/λ' was found to decrease slowly at first and then more rapidly as the exciting beam became more penetrating.

Prof. BRAGG congratulated the author on his interesting experiments, and said he could not see any satisfactory explanation of them on the pulse theory.

A paper on the "*Theory of the Alternate Current Generator*," by Professor LYLE, was read by Dr. RUSSELL.

The author points out that the theory of armature reaction as ordinarily discussed by electricians is unsatisfactory, as an important effect due to the mutual induction between the current in the field winding and the current in the armature circuit is neglected. To simplify the problem, the case of a simple ironless single-phase alternator is first discussed. The magnetic field, supposed uniform, is due to the current in a fixed coil connected with a source of constant electromotive force, and the armature is a coil of wire rotated in this field with constant angular velocity. In these circumstances, we may suppose that the mutual inductance between the two circuits varies in accordance with the harmonic law. The differential equations which determine the values of the two currents are easily written down, but their solution presents difficulty. The author gives a method of getting the complete solution. He first assumes that both the currents can be expanded in Fourier Series. He then applies a novel vector method and obtains equations to determine the value of the harmonic of any order in terms of the constant term in the field current. The operators in these equations are infinite determinants, but he shows how these can be readily reduced to continued fractions. In practice, the resistance of the exciting circuit is small compared with its inductance, and thus the time constant is large. The continued fraction operators therefore rapidly become recurring, and so the equations giving the solution are simple.

The results prove that only odd harmonics appear in the expression for the armature current, and only even harmonics appear in the expression for the field current. The frequency of the induced ripple superposed on the exciting current is therefore double the fundamental frequency. The interesting fact is proved that this ripple is asymmetric; that is, the positive half of the wave is of a different shape from the negative half. A simple geometrical method of obtaining the solution is also given.

The author next takes into account the effects of hysteresis and eddy currents. This he does by means of the permeability operators, the use of which he explained in the *Phil. Mag.* for January, 1905. The magnetic leakage of the armature is also taken into account. As a practical illustration of the method, the operation of a small two-pole alternator when supplying a non-inductive load is predetermined. A diagram is given showing the exact shape of the current wave in the armature, the ripple superposed on the exciting current, and their relative phase displacement.

The action of "dampers" in diminishing the heat-losses in the field circuit and the theory of the synchronous motor are also discussed.

Mr. W. DUBDELL expressed his interest in Prof. Lyle's paper, and remarked that the results which he had obtained were in accord with experiments made by himself and Dr. Marchant some years ago.

Dr. RUSSELL congratulated the author on having obtained such instructive solutions of the differential equations which determine the value of the armature and field currents in a simple generator. The subject of armature

reaction has been carefully studied by electrical engineers, and the literature of the subject is quite extensive. He referred in particular to the study made by Prof. Blondel in 1900 of the ripples in the exciting current of a two-phase and a three-phase alternator. It was well-known that in a single-phase machine the frequency of the ripple superposed on the exciting current by the alternate magnetising and demagnetising effect of the armature current was double the frequency of the armature current. This ripple disappears at no load, but in practice the ripples at no load are often very marked owing to pulsations of the reluctance due to slots in the armature. The latter ripples are much less pronounced at full load as the load circuit acts like a damping-coil; but new ripples due to the armature reaction appear, causing a distortion of the wave-form. As a rule, electrical engineers assumed the existence of a sine wave of armature current and then investigated the ampere-turns to be added or subtracted from the field-coils so as to neutralise the magnetising or demagnetising effect produced. In this connection Blondel's two reaction method was extensively used as it enabled approximate values to be rapidly obtained. The effect of the reaction on the wave-form of the machine, however, had been practically neglected, and Professor Lyle deserves great credit for his solution. In connection with the parallel running of turbo-alternators it was important, and the theory deserved careful study by engineers. The speaker thought that "dampers" were mainly used to prevent phase-swinging. He agreed with Professor Hopkinson that a similar effect might often be more economically produced by putting more copper on the field windings. The difficulties that arose in connection with perfecting the theory of synchronous motors arose mainly from the difficulty of taking hysteresis into account in the mathematical equations. He thought that Professor Lyle's work in this direction was most valuable.

Prof. L. R. WILBERFORCE exhibited a galvanometer or the Broca pattern suitable for general use in elementary laboratories.

NOTICES OF BOOKS.

An Introduction to the Science of Radioactivity. By CHARLES W. RAFFETY. London, New York, Bombay, and Calcutta. Longmans, Green, and Co. 1909.

ALTHOUGH there is nothing strikingly new in the treatment of the subject of this book, the author has extracted from other literature what is likely to prove interesting to the average reader, and has made a very readable whole of it. For the general reader the book will have many attractions, not the least being the clearness of the style and the conciseness of the language. Of the three parts into which the book is divided—descriptive, theoretical, and practical—the last perhaps the least satisfactory. Although intended to suggest some experimental work illustrating the production of rays and the properties of radio-active substances, the directions are often too vague to be of much practical use, and constitute not much more than hints for workers who have already had some experience in the manipulation of active compounds. The first part of the book contains a discussion of the properties and nature of the α , β , and γ -rays, while in the second part the theory of atomic disintegration is carefully and lucidly explained. An appendix gives a very brief tabular summary of the text, which will be found useful to clear up any obscurities which may arise owing to the comparative complexity of the subject from the point of view of the untrained reader.

L'Industrie des Parfums. ("The Perfumery Industry"). By M. OTTO. Paris: H. Dunod and E. Pinat. 1909.

A VERY complete account of the chemistry of perfumes is given in this book. The elements of organic chemistry

are first discussed, some account of stereo-chemistry being included, and in fact the first chapter is practically a short course of organic chemistry specially suited for those who are interested in the perfumery industry. Methods of analysis are treated very shortly in this introductory section, and the different perfumes are classified according to chemical constitution. The chief natural perfumes and essential oils are then studied in detail, the localities from which they are obtained being shown on numerous maps, while the physical and chemical properties and methods of extracting each substance are entered into fully. Modern methods of preparing artificial perfumes are treated in the last section.

The Manufacture of Explosives. Twenty Years' Progress. By OSCAR GUTTMAN. London and New York: Whitaker and Co. 1909.

THIS volume contains four Cantor lectures delivered by the author before the Royal Society of Arts in November and December, 1908. The period which they cover has been one of extraordinary fruitfulness in investigations relating to the use of different types of compounds as explosives, and the compression of all the notable advances which have been made into four lectures was by no means an easy task. The author's unique experience and knowledge have, however, enabled him to produce a valuable summary of the progress of the last twenty years' in the manufacture and application of explosives. He touches upon all the recently patented substances, and gives some account of modern improvements in their manufacture; his remarks upon the safety of various materials under different conditions will be of value to manufacturers, who will also be interested in the expression of his opinions upon the explosive of the future. This he believes will contain a nitro derivative of the aromatic series, possibly used in conjunction with nitroglycerin.

The Dyeing and Cleaning of Textile Fabrics. By F. A. OWEN, B.S. Based partly upon the Notes of H. C. STANDAGE. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1909.

THE chief value of this book will be to the amateur who aspires to dispense with the services of dyers and cleaners and do his own renovating at home. For this purpose recipes for dyeing small articles and inconsiderable quantities of silks and wools are given, with directions how to apply the dyes, and a very useful summary of dyestuffs is added. This summary gives brief instructions for using the dyes, and includes a list of dye-stuff manufacturers and their agents. The cleaning of all kinds of articles and the removal of stains of different origin are also treated, and the book contains many recipes which will be appreciated by the housewife. These include directions for the preparation of all kinds of soaps, and in addition some hints are given on such domestic matters as the washing and ironing of clothes. As a work of reference the book would no doubt be found useful in the home.

Heat and other Forces. By Colonel W. F. BADGLEY, A.I.C.E., F.R.G.S., F.R.M.S. London: King, Sell, and Olding, Ltd. 1909.

THE aim of this book is to prove that heat is not vibration of material nor of ether, and that matter is not composed of molecules in motion, but of particles in absolute contact. To arrive at this proof the author has to ignore many phenomena which are generally accepted as actually occurring, and has to find explanations for experiments which are sometimes diametrically opposed to the conclusions scientific men draw from them. It needs only a very short examination of the book to discover that the author's knowledge is superficial and his reasoning loose. For instance, from the fact that both earth and moon were once part of the sun he deduces that all three must have the same composition. Add to this lax reasoning a particularly careless and inaccurate wording, as, for example,

when he speaks of the heat given up by a piece of radium as one and a-half degrees centigrade, or of inertia being made up of weight and friction, and the value of the book as a serious contribution to science can very justly be estimated. It is not surprising to find that the metric system finds no favour in the author's eyes, his opposition being partly based upon the relative weakness in the powers of calculation of Continental and American peoples who have adopted the system.

Outlines of Physical Chemistry. By GEORGE SENTER, Ph.D., B.Sc. (Lond.). London: Methuen and Co. 1909.

As an elementary text-book of physical chemistry at a very moderate price this book can be recommended for the use of students, more especially for those who are preparing themselves for a career in electrical engineering. The mathematics used are very elementary, perhaps even unnecessarily so for the class of student for whom the book is intended, a knowledge of logarithms representing the limit of what is expected of him. Certain subjects, such as, for instance, theories of solution, electrical conductivity, which are important for those who are studying physical chemistry as a means to an end, and who hope to specialise in other branches of scientific work, are treated at length, and the reader should be able to acquire from the book a very fair knowledge of electro-chemistry in its most recent developments. Although not intended to be a laboratory manual, the book contains suggestions for suitable practical work on the subject of almost every chapter, and for some of the simpler experiments sufficiently full details are given to enable the student to perform them without reference to other works.

Heat Energy and Fuels. By HANNES V. JÜPTNER. Translated by OSKAR NAGEL, Ph.D. New York: McGraw Publishing Company. 1908.

AN edition in the English language of Prof. v. Jüptner's valuable work on chemical engineering will be received gratefully by practising engineers and instructors in this country. The work has been issued in German in four parts, of which the first deals with Heat Energy and Fuels. The book is very systematic, a special feature being the many tables and tabular statements containing information which it is often difficult to find. The chapters are usually short, but the subject is not treated in outline only, some considerable amount of detail being rendered possible by the admirable classification and division of the text under suitable headings. The measurement of high temperatures by pyrometers of different type is well treated, and throughout the book suggestions are made for practical exercises which could with advantage be performed by the student who was using the book as a text-book of chemical engineering.

Elektrolytische Zähler. ("Electrolytic Meters"). By Dr. KONRAD NORDEN. Halle-a-S.: Wilhelm Knapp. 1908.

SINCE Edison's first patents for electrolytic meters were taken out nearly thirty years ago, although meters of various types have necessarily been largely used, those on the electrolytic system have not been improved as much as mechanical instruments, and the former may to a certain extent be regarded as still in the experimental state. The author of this monograph, feeling that in the near future they will be more generally employed and the construction of them will be perfected, thought it worth while to summarise the present state of their development, clearly marking out what has been done and what still remains to be done. At the same time he endeavours to do more than give a historical account of the subject, and explains the directions in which further experimental and constructive work seems likely to lead to satisfactory results. He discusses very lucidly the standard to which an electrolytic meter should attain, and examines every type o

instrument which has been constructed, enumerating with perfect impartiality the merits and demerits of each. The various laboratory voltmeters and the evolution of the meter from them are treated in the first part of the book, in which the author carefully explains the necessary differences between the two instruments.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Berichte der Deutschen Chemischen Gesellschaft.

Vol. xlii., No. 5, March 13, 1909.

Potassium Perborates.—C. von Girsowald and A. Wolokitin.—Only two well-characterised potassium perborates appear to exist, $2\text{KBO}_3 \cdot \text{H}_2\text{O}$ and $2\text{KBO}_3 \cdot \text{H}_2\text{O}_2$, and the other substances which have been described appear to be mixtures of these with one another or with potassium metaborates. The former is prepared by dissolving boric acid and caustic potash in water, and adding hydrogen peroxide in the cold. The solution is filtered, and the potassium perborate precipitated with methyl alcohol. It corresponds to the sodium salt in properties. $2\text{KBO}_3 \cdot \text{H}_2\text{O}_2$ is prepared by mixing an aqueous solution of potassium metaborate with hydrogen peroxide solution. It is somewhat less soluble in water than the former salt, but otherwise resembles it. The antiseptic properties of both salts are more marked than those of pure boric acid and potassium chlorate.

Preparation of Ethylene from Carbon Monoxide and Hydrogen.—Georg Orlow.—Lumps of coke were treated with nickel nitrate, dried, and treated with ammonium palladium chloride solution, again dried and ignited. They were then ignited in a copper tube in a current of methyl alcohol, and then a mixture of about equal volumes of dried hydrogen and carbon monoxide was passed over them. Ethylene was found in the exit gases. Apparently the carbon monoxide is reduced by the nickel to the methylene group, and this then condenses to form ethylene, $\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_2 + \text{H}_2\text{O}$, $2\text{CH}_2 = \text{C}_2\text{H}_4$. The formation of ethylene is not in agreement with the thermochemistry of the reaction, according to which methane should be formed.

Crotonic Acid Anhydride.—Andreas Luniak.—The anhydride of crotonic acid can be prepared by the action of crotonyl chloride on the sodium salt of crotonic acid. The crotonyl chloride may conveniently be obtained by treating crotonic acid with phosphorus trichloride. Crotonic acid anhydride is a colourless liquid with a peculiar smell.

Behaviour of Fluorine towards Nitrogen, Oxygen, and Chlorine in the Arc and Induction Spark.—Otto Ruff and Julian Zedner.—The authors describe different forms of apparatus in which fluorine and mixtures of gases containing fluorine can be heated in the electric flame arc or by induction sparks. In this apparatus mixtures of fluorine with nitrogen, oxygen, and chlorine were heated. The investigation of the gases does not show that fluorine reacts with these elements. Although compounds may be formed at very high temperatures only very small quantities could result under the conditions of the experiment.

MISCELLANEOUS.

Wolcott Gibbs Memorial Lecture.—The above lecture will be delivered by Prof. Frank Wigglesworth Clarke at the Ordinary Scientific Meeting of the Chemical Society on Thursday, June 3rd, at 8.30 p.m.

Royal Institution.—On Tuesday next, May 18, at Three o'clock, Prof. J. Garstang delivers a lecture at the Royal Institution on (1) "Monuments of Egypt and Asia Minor," being the first of a course of two Lectures on "The Hittites"; and on Saturday, May 22, Dr. W. H.

R. Rivers begins a course of two Lectures on "The Secret Societies of the Banks' Islands." The Friday Evening Discourse on May 21 will be delivered by the Hon. Ivor C. Guest on "Afforestation," and on May 28 by Dr. Emerson Reynolds on "Advances in our Knowledge of Silicon as an Organic Element." An extra Friday Evening Discourse will be delivered on June 18 by Mr. A. Henry Savage Landor on "A Recent Visit to the Panama Canal."

Food Congress at Paris, 1909.—The highly successful Congress in connection with the suppression of frauds in Food, and which was inaugurated last year at Geneva, will be succeeded by a similar Congress to be held in Paris during October of the present year. The Congress is under the auspices of the Society of the White Cross of Geneva, which is so ably presided over by Mr. C. H. Vuille of that city, and it is contemplated that the forthcoming Congress will far exceed in numbers present those who attended at Geneva. It may be remembered that these numbered about 400 delegates, representing twenty-nine different nations, and that the deliberations were followed with great interest throughout. At the forthcoming Congress at Paris, the principal object will be to define such methods as will prevent the fraudulent adulteration of food, but there will also be sections devoted to chemical products, pharmaceutical preparations, mineral waters, and similar substances. The list of foods alone which will be discussed is an imposing one, and includes all the various well-known products used in our domestic economy. There will be two principal sections in connection with the Congress, namely, the technical section and the industrial one, and it will be for the adherents to those two sections to define clearly what purity of the various substances discussed really means. It is obvious, also, that the combination of technical and scientific men along with actual producers is likely to lead to clear and practical definitions. The Congress will be of a highly important character to every one connected with the Food Supply; and it is anticipated that there will be a considerable representation of British interests in connection with the technology and science of the subject as well as in connection with agriculture and manufactures of food products. It is desirable that those who intend to participate in the Congress, either by the appointing of delegates or as individuals, should make up their minds pretty soon so that proper arrangements may be made. Any other information can be obtained from Mr. LOUDON M. DOUGLAS, College of Agriculture, Edinburgh. The General Secretary is Mr. ROBERT FAZY, 42 Rue du Rhone, Geneva.

MEETINGS FOR THE WEEK.

TUESDAY, 18th. - Royal Institution, 3. "The Hittites (1) Monuments of Egypt and Asia Minor," by Prof. J. Garstang.

— Royal Society of Arts, 4.30. "Canada as a Field for British Investment," by J. Obed Smith.

WEDNESDAY, 19th. - Royal Society of Arts, 8. "Railway Development in China," by Arthur J. Barry.

— Microscopical, 8. "Recent and Fossil Foraminifera of the Shore-sands of Selsey Bill, Sussex" (Part II.), by E. Heron-Allen and A. Earland. "New Illuminator for the Microscope," by J. W. Gordon. Exhibition of Pond Life.

THURSDAY, 20th. - Royal Institution, 3. "Newfoundland," by John G. Millais, F.R.S.

— Chemical, 8.30. "Action of Nitric Acid on the Ethers of Aromatic Hydroxyaldehydes," by A. H. Salway. "Isolation and Synthesis of *p*-Hydroxyphenylethylamine, a Water-soluble Active Principle of Ergot," by G. Barger. "Nitrodioxylyl (Nitrotetramethyldiphenyl)," by A. W. Crossley and C. H. Hampshire. "Ammonium Perhalides," by F. D. Chattaway. "Studies in Asymmetric Synthesis. Part VIII. The Asymmetric Synthesis of *l*-Mandelic Acid," by A. McKenzie and H. B. P. Humphries. "Condensation of Acetone and Hippuric Acid," by W. H. Perkin and J. L. Simonsen. "Sodium Sulphite," by H. Hartley and W. H. Barrett.

FRIDAY, 21st. - Royal Institution, 9. "Afforestation," by Hon. Ivor Churchill Guest, M.P.

SATURDAY, 22nd. - Royal Institution, 3. "The Secret Societies of the Banks' Islands," by W. H. R. Rivers, F.R.S.

THE CHEMICAL NEWS.

VOL XCIX., No. 2582.

MATHEMATICALLY HARMONISING THE ELEMENTS.

SOME CHEMICAL REGULARITIES.

By F. H. LORING.

IN the CHEMICAL NEWS of March 26 (vol. xcix., p. 148) I described a method of harmonising the atomic weights by marshalling the elements on elliptical curves. No attempt was then made to indicate any chemical regularity except as regards the inert gases, which were picked out by two circles where they intersected the ellipses.

The symmetrical distribution of the inert gases, which appears when the elements of the curves are arranged in tabular form (*vide* p. 150), suggests that some further regularities may be found; that this is the case will be seen from the following notes.

An Acidic Regularity.—If a list of the clearly defined acids be made—namely, hydrochloric, hydrofluoric, boric, phosphoric, vanadic, hydrobromic, permanganic, selenic, niobic, arsenic, silicic, germanic, telluric, chromic, titanio, sulphuric, per-rhodic, carbonic, stannic, hydroiodic, molybdic, antimonic, tantalio, and perhaps auric, and one or two others, the elements of which function in producing both basic or acidic oxides, or yield feeble acids—the acidic elements will be found to be uniformly distributed throughout the table on p. 150, above referred to. This table is substantially reproduced below with the principal acidic elements enclosed in brackets, these being arranged uppermost in each column to bring out the regularity in question.

Four and five blanks are shown in the first and second groups respectively, assuming that four elements belong to each intermediate curve of the second group. The third grouping, which is not attempted, would probably take tungsten (tungstic acid), osmium (osmic acid), platinum (platinic acid), lead, bismuth, thorium, uranium, radium, ionium, &c., leaving many blanks. To the second group probably belong holmium (162), neoytterbium (172), decipium (171), and lutecium (174), leaving only one unfilled space. Into the first group gallium (70) and two newly discovered elements by Ogawa (College of Science, &c., Kyōto) may fit. One, provisionally named "nipponium" (Np), which gives a higher acidic oxide similar to molybdenum trioxide, has a probable weight of about 100; the other one, also yielding a higher acidic oxide, has an equivalent of about 16.7, but its valence has not been fixed (CHEMICAL NEWS, vol. xcvi., p. 249, and p. 261). While it is difficult to make proper use of some of the rare elements in a classification of this kind, owing to the uncertainty or meagreness of the data, the incandescent gas-mantle industry has led to the investigation of many rare elements, with the result there is a surprisingly large amount of very accurate data now available.

Since the weights of most of the elements have not been determined to the second place of the decimals, the close proximity of curves Nos. 1 and 2, as well as of Nos. 5 and 6, Nos. 10, 11, and 12, make it difficult to form any conclusive opinion as to whether all the elements of the two groups tabulated are correctly assigned to the curves, notwithstanding this regularity.

It is obviously difficult to classify all the elements in terms of acidity, as the line of demarcation is not definite in every instance, but an inspection of the table will make it clear that the acidic elements (using this term advisedly) are very evenly scattered through the table.

A Peroxide Regularity.—Referring to the same table, a striking regularity is revealed by the non-acidic elements that give peroxides, e.g., sodium (NaO₂), potassium (K₂O₄), zinc (ZnO₂), &c., which are enclosed in parentheses.

Curve Nos.									
1.	2.	3.	4.	5.	6.	7.	8.	9.	
A									Kr
[Cl]									[—]
[F]									[Ge]
[B]									[Si]
[Al]	[—]	[P]	[V]	[Br]	[Mn]	[Se]	[As]		Mg
Be	Li	Fe*	Cu	—	Co*	[Nb]	Yt		Ni*
[H]	(Na)	(K)	(Zn)	(—)	(Rb)?	(Sr)	(Ru)		(Ag)
FIRST GROUP.									
10.	11.	12.	13.	14.	15.	16.	17.	18.	
[Fe]									[—]
[Cr]									[Au]
[I]									Ir
[S]	[C]	[Sn]	[I]	[Mo]	[Sb]	[—]	[Ta]		Eu
[Rh]	O	—	Cd	Gd	[Er]	—	Tu		Dy*
Sc	Ne	Pd	In	Xe	(Pr)	Nd	Y		Hg
(Ca)	[(Z)]	(Ba)	(Cs)	(Li)	(Tb)	(Ce)	(Sa)		(—)
SECOND GROUP.									

Notes.

When some uncertainty attaches to the question of whether an element gives a peroxide or not, the benefit of the doubt is given in favour of the tabular regularity. This seems admissible in support of the scheme until more accurate weights are obtainable, when a rigorous test as to its truth can be made.

Baxter and Coffin (*Zeit. Anorg. Chem.*, 1909, lxii., p. 50) give the revised weight of arsenic as 75.02, 74.96, or 74.92, according as the fractions for silver are taken as 0.93, 0.88, or 0.85 respectively. The value 74.98 is concordant with silver taken at 107.90, and this figure is established by curve No. 8.

In the case of chromium, Baxter, Muller, Hines, and Jesse, jun. (*Journ. Am. Chem. Soc.*, May, 1909), have found the weight of this element to be 52.06, 52.01, or 52.98 according to the above-named fractions for silver. Consequently, pending further determinations, Cr must be assigned to curve No. 12, if its value is 52.03, to agree with silver taken at 107.90.

The Magnetic Elements.—These elements are shown by an asterisk, and they fall on the 3rd, 6th, 9th, and 18th curves, indicating that the 12th and 15th curves should carry similar elements. Inasmuch as only four pronounced magnetic elements are at present known, this inference is not justifiable. Shukoff (*Comptes Rendus*, 1908, cxlvi., 1396) has obtained a strong magnetic oxide of chromium by heating CrO₃.

Specific Heat Sequence.—The position or sequence of the elements on the curves appears to bear a relation to their specific heats, and the close inverse relation of specific heat to atomic weight may be explained by virtue of this regularity rather than by the assumption that it follows as a consequence of the atomic weight, or according to the law of Dulong and Petit. Referring to curve No. 1 the following sequence in specific heats at 0° C. is noticeable:—

Argon, 20—90° C. (Dittenberger)	0.1233
Chlorine, 13—202° C. (Regnault)	0.1241
Aluminium, 15—185° C. (Tilden)	0.2189
Fluorine	—
Boron, 0—100° C. (Moissan and Gautier) ..	0.3066
Hydrogen, 21—100° C. (Wiedemann)	3.410

By interpolation, gaseous fluorine should be about 0.25. Other examples might be given.

It is noteworthy that the position of copper (specific heat 0.0936) on the upper division of curve No. 4 is exactly the same as that of zinc (specific heat 0.09356) on the lower division, and, consequently, their specific heats should be identical, although their atomic weights are not quite the same.

The Theory of Satellites.—This idea, due, I believe, to Wetherell, which I adopted to get over a difficulty in regard to nitrogen and beryllium (glucinum) is too hypothetical to be seriously entertained without experimental evidence, although there is astronomical evidence of a body (gas) having an atomic weight below that of hydrogen. The weight of the satellite given in my previous article, namely, 0.2684, should be regarded as a roughly approximate figure. A large scale drawing was made, the extreme accuracy of which might easily be questioned. Moreover, the value of this figure is alterable according to the weight taken for nitrogen, and therefore involves suppositions that are not sufficiently well-founded. The postulate that iodine carried such a satellite is to some extent warrantable, since recent determinations of tellurium and iodine have, I believe, confirmed the inverse position of these elements in Mendeleeff's periodic table. Further, a satellite may give iodine its halogen properties, just as the oxygen or nitrogen of NO_2 gives in this example a body closely allied to the halogens, yet its component elements, N and O, are individually quite different. This mode of reasoning will be more apparent if a study be made of the table given in my previous article in a footnote on page 148. Granting that the satellite theory is true and that the minute body could be separated from iodine, the resultant element would probably be totally different, even if it did not break up into two or more atoms.

In conclusion, it should be noted that these various systematic attempts at harmonising the elements, involving tables in which some rearrangement is effected, are by no means final. Each assemblage is made with the view of dealing with one or two chemical attributes apart from all others. It is a process of sorting in which those elements having pronounced qualities are singled out first. Other attributes seem to be foreshadowed, and the tendency of each curve to carry a definite "assortment" seems fairly well established. It should also be noted that Nb may belong to curve No. 9, and that Mo may change places with I, and Er may fill the upper gap shown on curve No. 16. There is some indication that the curve intersecting cobalt and manganese should be deleted and a new one established near to the one at present intersecting sodium and lithium. *This change would make the two groups of curves identical in the character of their spacing as measured on the +0.8 line.* In that case, sodium might be expected to belong to the third curve and lithium to the second, whereby the existence of the latter as a peroxide would be justifiable. Rubidium would have to be assigned to the curve intersecting strontium, selenium, and niobium. These, or other changes, will doubtless be necessary when the weights of the elements become more accurately known.

7, Doughty Street, London, W.C.,
May, 1909.

AN EXTRACTION APPARATUS FOR PLANT PRODUCTS, &c.

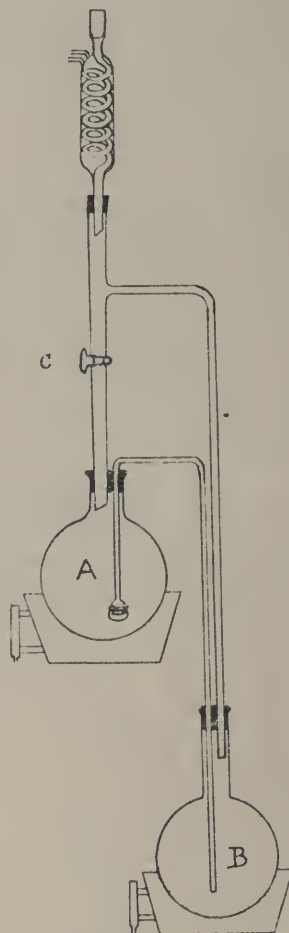
By S. J. M. AULD, D.Sc., Ph.D., and SAM'L. S. PICKLES, D.Sc.

THE apparatus, of which a figure is given, has been found very useful for the extraction of large quantities of material with solvents, e.g., the extraction of oil from oil-seeds, resins, and other extractive matter from ground woods, leaves, grasses, &c. It possesses the following advantages over the apparatus generally used:—(1) Larger quantities of material can be dealt with; (2) the extraction is effected at the boiling-point of the solvent; (3) the solvent is rapidly and continuously recovered in the same apparatus, thus dispensing with prolonged distillation processes in separate vessels.

The apparatus consists of a large bolt-head flask fitted with a two-holed stopper. Passing almost to the bottom

of the flask is a fairly narrow tube carrying at its lower extremity a thistle funnel firmly packed with cotton-wool, and covered with a piece of fine muslin or cotton-cloth. On leaving the flask this tube is bent twice at right angles, and forms a syphon, the lower arm of which communicates with a second flask at a lower level than the first. The other tube passing from the extraction flask is connected with a condenser, and carries a side tube which communicates also with the lower flask. A tap is fitted on this tube between the extraction flask and the side tube.

The material to be extracted is placed in the flask A, and the solvent is added until the flask is about two-thirds full. The contents are then heated to the boiling-point of the



solvent, the stopcock c being open. When the solvent has become saturated the cock c is closed momentarily, and the solution passes through the syphon tube into the flask B, any solid particles being held back by the cotton-wool filter.

The tap c is opened as soon as the syphon is set, and the solvent is distilled from the flask B, entering the extraction flask through the upper side tube. The aperture in the stopcock c should be as large as possible; in fact, for most solvents the tap may be dispensed with, and an indiarubber joint inserted in its place. The tube can then be temporarily closed by pressure with the fingers when it is required to force the solvent into B. Experiments are being made with a view to rendering the process quite automatic.

THE ANALYSIS OF ORES OF TANTALUM.

By EDWARD S. SIMPSON, B.E., F.C.S.

I HAVE read with much interest the paper of Mr. W. B. Giles, F.I.C., on "Tantalum, Niobium, and Titanium," appearing in the *CHEMICAL NEWS* (vol. xcix., p. 1 *et seq.*). My experiments upon minerals containing tantalum and niobium having led, in some instances, to quite different results to those experienced by Mr. Giles, a few notes thereon will probably be found of some value to others interested in these metals.

After six months of experimenting with various methods for the analysis of local tantalum ores, which are characterised for the most part by an almost total absence of titanium but by a variable and sometimes large percentage of cassiterite, a method was evolved which has given considerable satisfaction. This was published in 1906 in *Bulletin* 23 of the Geological Survey of Western Australia, in the laboratory of which (which I have the honour to direct) it is still, with some minor modifications, in use. This method has been adopted at the Royal Test Office of the Technical High School, Berlin, the director of which states in a note appended to an assay certificate issued in December, 1907, that whilst this method cannot claim a greater exactness than perhaps 1 per cent for the separated oxides—E.S.S.] "genauere Verfahren sind nicht bekannte." The percentage of combined oxides ($\text{Ta}_2\text{O}_5 + \text{Nb}_2\text{O}_5$) obtained by this method can be relied upon to be accurate to one-tenth of 1 per cent in the absence of appreciable amounts of TiO_2 .

The method, founded upon the work of Marignac and others, is described in detail on pages 72—74 of *Bulletin* 23 of the Geological Survey of Western Australia, which can be obtained at the offices of the Agent-General for Western Australia. Briefly, it consists in a fusion of the ore with caustic potash in a nickel or silver crucible, extraction of the melt with a limited amount of water, acidifying with a definite amount of hydrochloric acid, boiling to complete solution of bases, and diluting and further boiling to precipitate hydrates of $\text{Ta}_2\text{O}_5 + \text{Nb}_2\text{O}_5$. The mixed moist hydrates are dissolved in water, acidified with HF , and separated by adding KF , evaporating, and removing successive crops of crystals of K_2TaF_7 . The niobium in the final liquor is precipitated as hydrate, weighed as oxide, and subtracted from the mixed oxides determined on a second lot of ore, the tantalum oxide being given by the difference. Tin, iron, manganese, &c., are determined in the original filtrate from the mixed hydrates. After a little experience, if the details laid down in the original paper be followed carefully, no difficulty will be experienced in getting results for tantalum and niobium well within 1 per cent of the correct amount, which is the most we can expect in the present state of our knowledge of those metals and their compounds. The only detail in which a departure has been made from the original method is that an allowance is made of 2 mgrms. instead of 3.6 mgrms. of Ta_2O_5 for every 1 cc. of the liquor from which the final crystallisation of K_2TaF_7 has taken place.

It will be seen that the method outlined involves decomposition with caustic potash, a method utterly condemned by W. B. Giles on several grounds. I shall deal with these in detail, and point out how his unfortunate experience of this method may be entirely obviated. His first difficulty was with crucibles, being under the impression that only gold-lined platinum, silver, or iron crucibles could be used, and that the temperature of fusion must be so great as to destroy these rapidly. Next, he found the melt invariably crept over the edge of the crucible. Finally, he found that the fusion with alkali did not entirely convert the mineral into a compound readily soluble in water, but that acid salts insoluble in water were formed which required re-fusion. The secret of his lack of success is contained in the sentence (p. 1) which shows that, "starting with 5 grms. tantalite and 10 grms. of potassium hydrate," he obtained insoluble acid salts. Now, 5 grms.

of the Australian tantalite referred to contain, on the average, 3.4 grms. Ta_2O_5 , 0.7 grm. Nb_2O_5 ; whilst 10 grms. of his KOH contained 7.2 grms. K_2O . The ratio of molecules in his melt would be roughly $8\text{Ta}_2\text{O}_5 \cdot 2\frac{1}{2}\text{Nb}_2\text{O}_5 \cdot 77\text{K}_2\text{O}$. A readily soluble normal or basic tantalate might be expected to result from such a melt in spite of the 14 per cent of MnO to be converted into manganate, and the rapid absorption of CO_2 from the burnt coal-gas with which it is heated. However, both Mr. Giles' experience and my own has been that when only two parts of KHO to one part of ore is used, the result is imperfect decomposition and solution. The remedy is obvious, viz., increase the proportion of alkali. The proportions I invariably use are six parts of KHO to one part of mineral. Such a mixture melts readily at a low red heat to a mass completely soluble in cold water, except for the carbonates and hydrates of iron, yttrium, &c., which are in turn readily dissolved by subsequent acidification with a little HCl . With these quantities I found at a low red heat decomposition was complete with—

Manganotantalite	(Through 90 sieve) in 10 minutes.
Ferrotantalite ..	} " " 20 "
Euxenite	
Fergusonite ..	
Stibiotantalite ..	
Cassiterite	Finely ground in agate, 45 to 60 minutes.

This does away with all objections to this method on the score of imperfect decomposition and high temperature. The cost of the large amount of KHO would, in the manufacture of tantalum oxide on a commercial scale, doubtless be an objection, in which case a somewhat smaller proportion of alkali might be substituted, provided all CO_2 be kept out of contact with the melt. For analytical purposes and experiments on a small scale the cost of the alkali is negligible.

With regard to crucibles, I find a nickel crucible the most generally useful, and never use any other for the determination of Ta_2O_5 , Nb_2O_5 , and SnO_2 . The wear is not great at such a low temperature, and the nickel which goes into solution does not affect in any way the clean precipitation of the tantalum, niobium, and tin. For the estimation of the iron, manganese, yttrium, &c., in these minerals I invariably make the fusion in silver, which I find but slowly affected at a dull red, rejecting the precipitates of hydrated Ta_2O_5 and Nb_2O_5 in this case, as they are invariably contaminated with silver chloride and scales of metallic silver, and also the precipitate of tin sulphide mixed with silver sulphide. When antimony is present as in stibiotantalite, the whole of this metal is precipitated with the tantalum and niobium on boiling the dilute solution acidified with HCl . It is separated from the precipitate by digestion with ammonium sulphide, and re-fusing the residual metallic oxides and repeating the precipitation and digestion.

Creeping of the alkaline melt is put forward as a serious objection. Except in the first two or three experiments, I have never had a case of creeping, which can be entirely avoided by heating in the following manner:—Take a small sheet of $\frac{1}{4}$ inch asbestos millboard, and cut in it a circular hole of such a size that when the crucible is pressed tightly into it the bottom only projects through about a quarter of an inch. A single Bunsen burner will heat a small crucible so mounted to the requisite temperature, the bottom and the contained charge becoming dull red, whilst the lip of the crucible is too cool to permit of creeping. Much so-called creeping is due to small portions of the melt being projected against the never perfectly level under-side of the lid, whence they travel to one side and pass partly down the inside, partly down the outside of the crucible. This I avoid by placing each new lid in an agate mortar, and giving it a few smart taps with a rounded hammer. This makes it distinctly convex on the under-side, so that any projected portions of the fusion run toward the centre of the lid, whence they drop back into the melt.

All the results given in my paper on "Tantalum and Niobium in Australia," recently reprinted in the *CHEMICAL NEWS* (xcix., 49), and also those given in my paper on "Further Occurrences of Tantalum and Niobium in Western Australia," read last January before the Australian Association for the Advancement of Science, were obtained by the methods outlined above. My experience of the alkali fusion is that it is both the simplest and most accurate method of attacking native compounds of tantalum and niobium, no matter how complex. The presence, however, of an appreciable amount of titanium, whilst not affecting the results for tantalum nor rendering the manipulation more difficult, seriously complicates the separation of niobium. Under such circumstances the results for niobium appear to be low, those for titanium correspondingly high. This is a point requiring much further investigation. At present it would appear that when a dilute solution of mixed tantalate, niobate, and titanate of potash is acidified carefully to a point at which normally on boiling all the niobium and tantalum would be expected to be precipitated as hydrates, whilst the titanium would be held in solution as chloride, a soluble double chloride of titanium and niobium is formed, part of the niobium only being precipitated.

Geological Survey Laboratory,
Perth, Western Australia, March 31, 1909.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Annual Meeting, May 6th, 1909.

Sir A. GEIKIE, K.C.B., President, in the Chair.

THE votes of the Fellows present were collected, and the following candidates were declared duly elected into the Society:—Edward Charles Cyril Baly; Sir Thomas Barlow, Bart.; Rev. Ernest William Barnes; Dr. Francis Arthur Bather; Sir Robert Abbott Hadfield; Alfred Daniel Hall; Dr. Arthur Harden; Alfred John Jukes-Browne; Prof. John Graham Kerr; Prof. William James Lewis; Prof. John Alexander McClelland; Prof. William McFadden Orr; Dr. Alfred Barton Rendle; Prof. James Lorrain Smith; Prof. James Thomas Wilson.

Thanks were given to the Scrutators.

Ordinary Meeting, May 6th, 1909.

Sir ARCHIBALD GEIKIE, K.C.B., President, followed by Mr. A. B. KEMPE, Vice-President and Treasurer, in the Chair.

The SECRETARY made the following announcement:—

Colonel Sir David Bruce, who is in charge of the Sleeping Sickness Commission at present in Uganda, cabled to the Society on April 3rd, 1909, that the Commission had confirmed Kleine's observations on the period during which the Tsetse fly was capable of transmitting a Trypanosome infection.

A letter was received on April 30, 1909, from Sir David Bruce, dated Mpumu Chagwe, Uganda, April 3, confirming the telegram, and stating that the Commission had "repeated Dr. Kleine's experiments with *Trypanosoma gambiense* and *Glossina palpalis*, also with a Trypanosome of the dimorphon type and the same Tsetse flies, and found the flies infective after sixteen, nineteen, and twenty-two days."

Papers were read as follows:—

"*Reciprocal Innervation of Antagonistic Muscles.* Note XIV. *Double Reciprocal Innervation.*" By C. S. SHERINGTON, D.Sc., F.R.S.

"*Note on a Curious Property of Neon.*" By J. NORMAN COLLIE, F.R.S.

During some work with specially pure neon, it was noticed that as the gas escaped at ordinary pressure from a Topley pump up through the mercury in an inverted test-tube, each bubble glowed with a fine red glow. This property is very apparent if the neon is sealed up in a glass tube with mercury and the tube shaken violently. It was expected that the glow would always be produced when the tube containing the neon and mercury was shaken. This was found not to be the case, for it was noticed in many instances that after shaking for some time that the glow became very feeble. These tubes could at once be brought back to their original condition by allowing a discharge to pass through them from an induction coil. Sometimes, however, when a powerful discharge was passed through them, exactly the opposite effect is produced, and further sparking did not improve them. Platinum wires sealed through the ends of the tubes did not interfere with the property of glowing when shaken. Another tube was strongly etched inside with hydrofluoric acid, also without effect on the glow. Heating the tubes strongly did not destroy the effect, but, on the contrary, restored those tubes that had been spoilt by passing heavy electric discharges through them. It was found possible to produce, in this way, tubes that possessed the property of glowing only at one end, or glowing at both ends and not in the middle. The slightest trace of moisture entirely stops the glow. The tubes were filled at different pressures, varying from 120 to 200 mm. pressure, as it was found that the glow was as bright at these as at ordinary pressures, and a saving in neon was thus made.

"*The Properties of Colloidal Systems. I. The Osmotic Pressure of Congo-red and of some other Dyes.*" By W. M. BAYLISS, F.R.S.

Congo-red, although a colloid in the sense of not being diffusible through parchment-paper and exhibiting other colloidal properties, such as those dependent on surface effects, has an osmotic pressure equal to that which would be given if it were present in true solution in single molecules. The solutions are not resolvable into particles under the ultra-microscope.

The theoretical osmotic pressure is only to be obtained in the complete absence of extraneous electrolytes. Even the carbonic acid present in ordinary distilled water is sufficient to cause a marked fall in the pressure recorded.

The manner in which electrolytes produce this fall is by causing aggregation of molecules to form particles. This is the case whether acid, alkali, or neutral salt be in question.

The action of a stable colloid in protecting against the effect of electrolytes is shown to consist, in the cases of congo-red and of arsenious sulphide, in the production of minute aggregates, which, although causing fall in osmotic pressure by diminution of effective concentration, are not of sufficient size to precipitate. Hence, the protective power can only be regarded as a limited one, due probably to the formation of complex colloids.

The free acid of congo-red forms a deep blue colloidal solution when dialysed. This is easily resolvable under the ultra-microscope, but gives a definite and measurable, though small, osmotic pressure, about 14 mm. Hg for a 1 per cent solution. Assuming the kinetic theory to be correct, this means that the aggregates contain, on an average, twenty molecules.

Estimations of the molecular dimensions of this blue colloid were made on the basis of enumeration of the particles in unit volume by means of the ultra-microscope. The values found are larger than the accepted ones for water, &c., about 100 times in fact.

The whole of the results are capable of explanation on the assumption that colloidal particles possess the kinetic energy of molecules, but lend no support to any view that postulates the necessary presence of foreign electrolytes.

"The Origin and Destiny of Cholesterol in the Animal Organism. Part V. On the Inhibitory Action of the Sera of Rabbits fed on Diets containing Varying Amounts of Cholesterol on the Hæmolysis of Blood by Saponin. By MARY T. FRASER and J. A. GARDNER.

In an earlier paper it was shown by comparative estimations of the total cholesterol-content of the blood of rabbits that had been respectively fed on ether-extracted bran, and on the same extracted bran with the addition of known amounts of cholesterol, that some, at any rate, of the cholesterol absorbed found its way into the blood-stream. It seemed to us desirable to ascertain whether the cholesterol was absorbed into the blood-stream as such, or in the form of esters, or in both states; and also, whether the phytosterol of vegetable food can be utilised for the formation of cholesterol in the organism.

We made use of the observations of Hausmann, Abderhalden, and Le Count, who showed that, whereas cholesterol and phytosterol inhibit the hæmolytic action of saponin, their esters do not do so. A series of comparisons were made of the inhibitory action of sera of rabbits fed on extracted bran alone, on extracted bran, and, in addition, measured quantities of cholesterol, cholesterol esters, and phytosterol respectively on the hæmolytic action of saponin. Care was taken to keep the animals under strictly comparable conditions, and the different sets of hæmolytic experiments were carried out under diverse conditions. The following are the conclusions:—

1. When cholesterol is given with the food of rabbits, some is absorbed, and finds its way into the blood-stream as free cholesterol; only a portion of the total cholesterol given in the food is absorbed, the rest being excreted unchanged.

2. Cholesterol when in the form of esters undergoes hydrolysis in part, at any rate, during digestion, and appears in the blood-stream as free cholesterol.

3. When animals are fed on phytosterol this substance is in part absorbed, just as in the case of cholesterol, and appears in the blood-stream either itself or in the form of cholesterol.

"Some Effects of Nitrogen-fixing Bacteria on the Growth of Non-leguminous Plants." By W. B. BOTTOMLEY.

Bacterial cultures prepared from the algal zone of *Cycas* tubercles taken from below the surface of the soil always contain a species of *Azotobacter* associated with *Pseudomonas radicola*. Pure cultures of these organisms were obtained, and it was found that when they are growing in association there is an increased assimilation of free nitrogen.

Control 0.48 mgrm. N per 100 cc.
Pseudomonas alone 0.91 " "
Pseudomonas + *Azotobacter* 1.21 " "

In *Cycas* tubercles the bacteria live, usually imbedded in a slime, in the open spaces of the algal zone, and the projecting cortical cells presumably absorb the nitrogenous products of bacterial activity. Experiments made to ascertain to what extent, if any, a mixed culture of *Pseudomonas* and *Azotobacter* applied to the roots of other non-leguminous plants might influence their growth, the nitrogenous bacterial products being absorbed directly by the plant, gave the following results:—

Oats.—Pot experiments with oats grown in sand dressed with phosphates, potash, and lime. Treated pots watered once with the mixed culture solution. Average weight per plant—untreated, 0.42 gm.; treated, 0.74 gm.; increase, 0.32 gm. = 76 per cent.

Barley.—Field experiments on limed plots of 484 square yards. Seed only treated with bacterial culture. Yield per plot—untreated, 608 lbs.; treated, 691 lbs.; increase, 83 lbs. = 13.6 per cent. The barley from a treated plot also yielded a higher nitrogen content.

	Untreated.	Treated.
Mgrms. N per cent	1.55	1.76
Weight of 1000 corns, grms. . .	48.5	49.5
Mgrm. N per corn	0.75	0.87

Bulbs.—*Galtonia candicans* grown in sandy soil, manured and limed, 250 bulbs of equal size in each bed. Treated bed watered twice with mixed culture solution. Weight of bulbs when lifted and dried at end of season—untreated, 69 lbs. 3 ozs.; treated, 82 lbs. 1½ ozs.; increase, 12 lbs. 14½ ozs. = 18.6 per cent.

Parsnips.—Grown in garden soil, manured and limed. Half the bed watered once with mixed culture solution. Every parsnip grown in the bed included in the weights. Untreated, 63 roots weighed 22 lbs. 14 ozs.; average per root = 5.38 ozs.; treated, 65 roots weighed 26 lbs. 10 ozs.; average per root, 6.55 ozs.; increase per root, 1.17 ozs. = 21.7 per cent.

In all the experiments the soil was treated with lime before the mixed culture was applied.

CHEMICAL SOCIETY.

Ordinary Meeting, May 6th, 1909.

Prof. HAROLD B. DIXON, F.R.S., President, in the Chair.

MESSRS. H. C. Duckworth and I. H. Zortman were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Harold Edward Annett, B.Sc., Imperial Research Institute, Pusa, Behar, Bengal, India; Harold Arnfield, Peak Lodge, Buxton Road, Stockport; Alfred Charles Glyn Egerton, B.Sc., Chilton House, Thame, Oxon; Harry Essex, jun., 23, Bescot Street, Walsall; Andrew Sneddon Matchet, 13, Bute Gardens, Cathcart, N.B.; Norman Picton, B.Sc., Ph.D., 4, Pembroke Square, Kensington, W.; Herbert Charles Resker, B.A., The Sugar Works, Cossipore, Calcutta, India; Barth. Frere Sawbridge, B.A., Thelnetnam Rectory, Diss, Norfolk; Harry Sampson Wills, 59, Caldecott Road, Denmark Hill, S.E.; George James Woods, 2, Wellmeadow Road, Lewisham, S.E.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Hugh Garner Bennett, M.Sc.; Albert Riley Blackburn, B.Sc.; Henry Ernest John Bletcher; Frank Playfair Burt, B.Sc.; Walter Campbell; Howard Alfred Caulkin, B.Sc.; John Henry Chew; George Clarke; Reginald Cyril Herbert Cooke; George Stanley Cooper; Daniel Little Couch; Edward Gordon Couzens, B.Sc.; Henry Jermain Maude Creighton, M.A.; Philip Henry Crewe; Francis Clifford Dyche-Teague, B.Sc.; William Fowler; Charles James Grist; Egerton Hargreaves, M.Sc.; John Frederick Haws; Reginald Vernon Hickinbotham; Reginald Hopkinson, B.Sc.; Leonard Angelo Levy, B.A., B.Sc.; Harry Livesey; Floyd J. Metzger; Robert Müller; Frederick Leigh Okell; Robert Cecil Owen, B.Sc.; Norman Scott Rudolf, M.Sc.; Henry Llewellyn Smith, B.Sc.; Arthur Percy Strohmenger; Arthur Edwin Tate; Oswald John Dalgatty Thomas; Vernon James Tilley; Charles William Truelove, B.Sc.; Francis Lawry Usher, B.Sc.; George Bilderbeck Walker; John Webster; Robert William Wilson.

Of the following papers, those marked * were read:—

*115. "The Absorption Spectra of the Nitrates in Relation to the Ionic Theory." By EDWARD CHARLES CYRIL BALY, KATHARINE ALICE BURKE, and EFFIE GWENDOLINE MARSDEN.

The absorption spectra have been examined of nitric acid, and lithium, ammonium, and silver nitrates dissolved in alcohol and in water, and in various mixtures of these solvents. A comparison between the persistencies of the absorption band shown by N/10-solutions of lithium and ammonium nitrates shows that considerable variations occur as the percentage of water in the solvent is increased. For example, when the solvent contains 3 per cent of water a great decrease in the persistence of the absorption band is obtained as compared with that observed in pure alcohol and in alcohol containing 10 per cent of water.

On the other hand, the electrical conductivities of the N/10-solutions do not show any such variations, but only a steady increase with increase of water in the solvent. If, however, the limiting conductivities of the solutions be observed, it is found that a minimum is obtained when the solvent contains 3 per cent of water. Nitric acid differs from the metallic nitrates in that it shows no absorption band, and possesses very small electrical conductivity in pure alcoholic solution. The absorption band is developed, however, and the conductivity greatly increased with addition of water to the solvent. The limiting conductivity of the nitric acid solutions also shows a minimum with 3 per cent of water in the solvent. The results afford strong support to the theory of hydrated ions, the decrease in limiting conductivity and the absorption band observed with the solvent containing 3 per cent of water being doubtless due to the hydration taking place.

DISCUSSION.

Dr. SENTER asked if there was any evidence of a connection between the viscosity of the (mixed) solvent and the limiting molecular conductivity of the salts (compare Walden, *Zeit. Phys. Chem.*, 1906, lv., 217).

Mr. BALY said that the viscosity of the solvent seemed to exert only a very small influence. A mixture of alcohol and water in equal proportions showed a maximum viscosity, and although there was a minimum in the limiting conductivity of lithium nitrate near this point, neither silver nitrate nor ammonium nitrate showed any such minimum.

*116. "Studies in the Camphane Series. Part XXVI. Aryl Derivatives of Iminocamphor." By MARTIN ONSLOW FORSTER and TOM THORNLEY.

By condensing camphorquinone with aniline and some of its derivatives, aryliminocamphors have been obtained, and are found to possess unusually high specific and molecular rotatory power. Reduction of these compounds leads to the corresponding derivatives of aminocamphor, and is accompanied by profound depression of optical activity.

DISCUSSION.

Mr. P. W. ROBERTSON asked whether the coloured compound investigated dissolved with different intensities in different solvents, and if so, whether any relationship had been observed between the intensity of colour and the magnitude of the specific rotation.

*117. "Substituted Dihydrobenzenes. Part III. The so-called 1:1-Dimethyl-Δ²:5-cyclohexadiene of Harries and Antoni." By ARTHUR WILLIAM CROSSLEY and NORA RENOUP.

It was shown that the hydrocarbon described by Harries and Antoni (*Annalen*, 1903, cccxxviii., 88) as 1:1-dimethyl-Δ²:5-cyclohexadiene is in reality a mixture of the cyclohexadienes with the two methyl groups in the 1:2- and 1:3-positions, and probably does not contain any 1:1-dimethyl cyclohexadiene.

*118. "Diethoxythioxan; a Relation between the Refractive Power and Chemical Activity of some Sulphur Compounds." By HANS THACHER CLARKE and SAMUEL SMILES.

The interaction of sodium sulphide and chloroacetal in alcoholic solution furnishes acetal sulphide, which, on treatment with mineral acid, yields the cyclic sulphide, diethoxythioxan. The reactivity of the sulphur in the latter compound has been qualitatively studied, and it is found to be abnormally low in comparison with that of the same element in acetyl sulphide, benzyl sulphide, or saturated aliphatic sulphides. The authors consider that this depressed activity cannot be satisfactorily explained by steric hindrance, and, instead offer the hypothesis that the residual affinities of the unsaturated cyclic sulphur and oxygen partly saturate one another. A similar explanation may be applied to other compounds containing bivalent sulphur of abnormally low activity; for example, thiophen and phenyl sulphide. The refractivity of these sulphur

compounds also has been studied, and it was shown that a sub-normal reactivity is accompanied by abnormal refractive power. The thioxan derivative appears to possess a slight optical anomaly.

DISCUSSION.

Dr. SMILES, in reply to Mr. Baly, stated that attempts made with the object of preparing a hydrochloride of diethoxythioxan had been unsuccessful. No indications of the substance having the structure of a hydroxytetrahydrothiophen, as suggested by Dr. Forster, had been found, since acyl derivatives were unobtainable.

In reply to the President's question as to the action of oxidising agents, hydrogen dioxide was without action, but hot concentrated nitric acid destroyed the substance, sulphuric acid being formed.

119. "The Affinity Constants of Hydroxy- and Alkyl-oxy-acids." By ALEXANDER FINLAY, WILLIAM ERNEST STEPHEN TURNER, and GERTRUDE EMILY OWEN.

The affinity constants of phenylmethoxy-, phenylethoxy-, and phenylpropoxy-acetic acids and of α- and β-hydroxy-β-phenylpropionic acids have been determined at 25°. The values of the constant 100*k* were found equal to 0.074, 0.053, 0.048, 0.019, and 0.0040 respectively.

120. "The Chlorination of Acetanilide." By WILLIAM JACOB JONES and KENNEDY JOSEPH PREVITÉ ORTON.

When chlorinated by bleaching powder solution in acetic acid solution, acetanilide is converted into a mixture of *o*- and *p*-chloroacetanilides, of which the ortho-compound forms about 45 per cent, and not, as believed heretofore, less than 10 per cent. If the concentration of the acetic acid is less than 2 per cent, acetylchloroaminobenzene is formed together with the two chloroacetanilides; when the acetic acid is diluted to 0.25 per cent, the chloroamine forms the chief product.

The transformation of the acetylchloroaminobenzene yields a mixture of the isomeric chloroacetanilides in the same proportion. Chlorination of acetanilide by chlorine in glacial acetic acid solution gives a mixture of the two anilides, in which 30 to 32 per cent of the ortho-derivative is present.

121. "Esterification Constants of Substituted Acrylic Acids." (Part IV.). By JOHN JOSEPH SUDBOROUGH and MORTON JAMES PRYCE DAVIES.

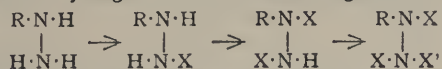
The constants, E_{MeOH}^{15} , have been determined for the following acids:—Acrylic, crotonic, α-methylacrylic, ββ-dimethylacrylic, angelic, tiglic, trimethylacrylic, isobutyric, α-methylbutyric, isovaleric, αβ-dimethylbutyric. The results indicate the retarding effect of the methyl groups, and also establish the retarding effect of the double linking in the αβ-position. The most remarkable point is that ββ-dimethylacrylic acid is esterified less readily than α-methylacrylic acid or tiglic acid.

122. "The Action of the Halogens on Aromatic Hydrazines." By FREDERICK DANIEL CHATTAWAY.

From the behaviour of the primary aromatic hydrazines when oxidised, it seemed likely that evidence of the formation of the mono-N-halogen substituted derivatives, which should be the first products of the interaction of primary aromatic hydrazines and any halogen, would be obtained if the reactions were carried out in presence of alkalis. Such compounds in presence of alkalis would be unstable, and might be expected to decompose into nitrogen, halogen hydride, and hydrocarbons. N-Dihalogen substituted derivatives, corresponding with the halogen acid additive products of diazonium salts, might be formed in small amount under favourable conditions and similarly decompose, yielding a monohalogen-substituted hydrocarbon. These expectations have been completely realised. When chlorine or bromine is brought into contact with a primary aromatic hydrazine in presence of potassium or sodium hydroxide, very vigorous action takes place, nitrogen is freely evolved, and the ·NH·NH₂ group is replaced by hydrogen; for example, by the action of bromine on

phenylhydrazine, *p*-bromophenylhydrazine, *o*-tolylhydrazine, and *p*-tolylhydrazine, there are produced benzene, *p*-bromobenzene, and toluene respectively. Any theory which attempts to explain the action of the halogens on primary aromatic hydrazines must therefore account for the production of hydrocarbons, mono-, di-, tri-, and tetra-substituted hydrocarbons, azo-derivatives, azoimides, hydrocarbons of the diphenyl series, diazonium salts substituted and unsubstituted in the aromatic nucleus, and the so-called diazonium perbromides.

It was explained how the complicated changes, which result in the formation of so many substances of such very different constitutions, all depend on a progressive substitution of hydrogen attached to the nitrogen, thus:—



followed by a breaking down or intramolecular rearrangement of the N-halogen-substituted hydrazines thereby produced.

123. "The Retarding Effect of Oxygen on the Rate of Interaction of Chlorine and Hydrogen." By DAVID LEONARD CHAPMAN and PATRICK SANSFIELD MACMAHON.

The authors have shown that when a moist mixture of chlorine and hydrogen containing a known amount of oxygen is exposed to light of constant intensity, the rate of formation of hydrogen chloride is, to a first approximation, inversely proportional to the amount of oxygen present. It is concluded from this result that the sensitiveness of a mixture of chlorine and hydrogen from which all oxygen had been removed would be infinite. The above quantitative relation was shown to be in harmony with the theory of inhibition advanced by Burgess and Chapman (*Trans.*, 1906, lxxix., 1433).

124. "The Colour of Aqueous Solutions of Violuric Acid." By FREDERICK GEORGE DONNAN and WILHELM SCHNEIDER.

Experiments were described which show that the conclusion of W. N. Hartley (*Trans.*, 1905, lxxvii., 1797), that pure aqueous solutions of violuric acid are colourless, is erroneous.

125. "An Examination of Irritant Woods. Part I. Chloroxylonine from East Indian Satinwood." By SAMUEL JAMES MANSON AULD.

From East Indian satinwood, derived from *Chloroxylon swietenia*, which has been reported to possess irritant properties, have been separated calcium oxalate, a peculiar protein compound, two inert resins, a fixed oil, and an alkaloid, $\text{C}_{22}\text{H}_{23}\text{O}_7\text{N}$. As the alkaloid cannot be identified with any known base, it is proposed to call it *chloroxylonine*. Chloroxylonine is a weak monoacidic base, and several of its salts have been prepared and characterised. It melts at $182-183^\circ$, contains four methoxyl groups, and is laevorotatory ($[\alpha]_D^{18} -9^\circ 18'$). The physiological action of chloroxylonine is being investigated by Prof. Cash, of Aberdeen, and in certain circumstances it seems capable of causing dermatitis similar to that ascribed to the wood itself.

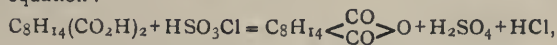
126. "Diazo-hydroxylamino-compounds and the Influence of Substituting Groups on the Stability of their Molecules." Part II. By NORMAN LESLIE GEBHARD and HERBERT BRYAN THOMPSON.

The various diazo-hydroxylamino compounds, prepared as described in the previous paper (*Trans.*, 1909, xcv., 767), have been examined with a view to determine the influence, due to position in the molecule, which the various substituting groups have on the stability of the compound considered. The action of bromine dissolved in an organic solvent, besides being a decomposing one, is of a substituting nature, and consequently of little use in determining the object in view; several new diazo-hydroxylamino-compounds were, however, prepared by its means. The action of hydrochloric acid in an organic solvent under comparable conditions for the various series of

isomeric substitution products was also investigated; it was found that the nitro-, bromo-, and carboxy-groups (but not the methyl group), when present in the ortho-position, greatly increased the stability, but as soon as the substituting group entered the meta- or para-positions the stability of the molecule decreased enormously.

127. "A New Method of Preparing Camphoric Anhydride." By JOHN PERCY EDGERTON.

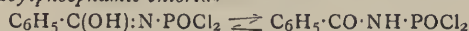
When camphoric acid is treated with chlorosulphonic acid a vigorous reaction takes place according to the equation:—



the principal product being camphoric anhydride, which can be quickly prepared as follows:—One hundred grms. of finely powdered camphoric acid are placed in a capacious flask fitted with a drying tube containing calcium chloride, and 33 cc. of chlorosulphonic acid are added; the mixture is then warmed on the water-bath, a further quantity of 16.5 cc. of chlorosulphonic acid is added, and the whole again warmed for about half an hour until the evolution of gas has practically ceased. The mass is then mixed with water, filtered through glass wool, and washed until free from acid. The camphoric anhydride crystallises from methylated spirit in fine needles, which, if not quite pure, can be obtained pure by a second crystallation.

128. "The Action of Phosphorus Pentachloride on Benzamide." By ARTHUR WALSH TITHERLEY and ELIZABETH WORRALL.

In the action of phosphorus pentachloride on benzamide different results are obtained according to whether the action takes place (1) in the cold without a solvent, or (2) in the cold with a solvent, or at 50° with or without a solvent. In (1) the result appears to be a mixture of phosphoryl chloride and α -chlorobenzimidide, $\text{C}_6\text{H}_5 \cdot \text{CCl} \cdot \text{NH}$, which gradually passes into benzonitrile and could not be isolated; in (2) α -dichlorobenzylphosphamic chloride, $\text{C}_6\text{H}_5 \cdot \text{CCl}_2 \cdot \text{NH} \cdot \text{POCl}_2$, is formed, which immediately loses hydrogen chloride, yielding α -chlorobenzylidenephosphamic chloride, $\text{C}_6\text{H}_5 \cdot \text{CCl} \cdot \text{N} \cdot \text{POCl}_2$, as an oil which solidified at low temperatures. The latter compound is comparatively stable at 50° , but decomposes at higher temperatures into benzonitrile and phosphoryl chloride; on exposure to atmospheric moisture, it yields fine transparent crystals of benzoylphosphamic chloride—



(m. p. 115°), which is practically unaffected by cold water. By treatment with aniline, α -chlorobenzylidenephosphamic chloride yields phenyliminophosphorylphenylbenzimidine, $\text{C}_6\text{H}_5 \cdot \text{C}(\text{NHPh}) \cdot \text{N} \cdot \text{PO} \cdot \text{NPh}$ (m. p. $227-228^\circ$).

Benzoylphosphamic chloride on treatment with aniline yields phenyliminophosphorylbenzamide,—



(m. p. 226°), which is soluble in sodium hydroxide, or benzoylaminoanilinophosphoryl chloride, $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{NH} \cdot \text{POCl} \cdot \text{NHPh}$ (m. p. 176°), according to the conditions of the reaction. The latter compound passes into the former by treatment with aniline, and does not yield the expected dianilino-derivative.

Benzoylphosphamic chloride readily undergoes replacement of the two chlorine atoms by hydroxyl on treatment with water in acetone solution, yielding benzoylphosphamic acid, $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{NH} \cdot \text{PO}(\text{OH})_2$ (m. p. $157-158^\circ$), which is readily soluble in water, and forms salts. The acid is rapidly decomposed by water at 100° , yielding phosphoric acid and benzamide, which crystallises out on cooling.

129. "Estimation of Iron by Permanganate in the Presence of Hydrogen Chloride." By JOHN ALBERT NEWTON FRIEND.

The author draws attention to the fact that the rate at which the permanganate is added to the ferrous solution greatly affects the value of the titration. It is suggested that the reaction takes place in two stages. First, a partial reduction resulting in the oxidation of some

of the iron, and the formation of an unstable perchloride of manganese. The latter substance then oxidises the ferrous iron according to the equation $\text{MnCl}_{(x+2)} + x\text{FeCl}_2 \rightarrow \text{MnCl}_2 + x\text{FeCl}_3$ until equilibrium is established.

If the directions given are rigidly adhered to, fairly accurate estimations of iron may be obtained in the presence of $\text{N}/4$ -hydrochloric acid.

130. "Contributions to the Chemistry of the Terpenes. Part. V. The Action of Chromyl Chloride on Terpinene and on Limonene." By GEORGE GERALD HENDERSON and WILLIAM CAMERON.

When chromyl chloride (2 mols.), largely diluted with carbon disulphide, is added to a similar solution of terpinene (1 mol.), a brown solid is formed which is decomposed by water, yielding a solution of chromic chloride and a brown oily liquid. The liquid oxidation product contains small quantities of cymene and of a ketone of the formula $\text{C}_9\text{H}_{12}\text{O}$, but is mainly composed of α -*p*-tolyl-propaldehyde, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CHMe}\cdot\text{CHO}$, and *p*-tolyl methyl ketone, $\text{COMe}\cdot\text{C}_6\text{H}_4\text{Me}$, both of which are derivatives of cymene. Hence the behaviour of terpinene towards chromyl chloride is different from that of pinene and of camphene, for whilst each of the latter hydrocarbons yields an additive product, $\text{C}_{10}\text{H}_{16}\cdot 2\text{CrO}_2\text{Cl}_2$, terpinene, on the other hand, is for the most part first oxidised to cymene, which then forms the compound $\text{C}_{10}\text{H}_{14}\cdot 2\text{CrO}_2\text{Cl}_2$, from which the aldehyde and the ketone are produced by the action of water.

It has also been found that the aldehyde and the ketone formerly prepared from limonene in a similar manner (*Trans.*, 1907, xci., 1871) are largely composed of α -*p*-tolyl-propaldehyde, and *p*-tolyl methyl ketone respectively, and therefore that limonene must likewise undergo at least partial oxidation to cymene when attacked by chromyl chloride under the conditions described.

131. "The Influence of Solvents on the Rotation of Optically Active Compounds. Part XV. Mixed Solvents." By THOMAS STEWART PATTERSON and HARVEY HUGH MONTGOMERIE.

The influence of two pairs of solvents on the rotation of an active compound was described, and the results were discussed in connection with the heat of mixture of the various compounds concerned, and also with reference to the discrimination of compounds in solutions.

132. "Optically Active Reduced Naphthoic Acids. Part IV. Comparison of the Rotatory Powers of the Di- and Tetra-hydronaphthoic Acids with those of Phenylallylacetic, α -Phenylvaleric, β -Phenyl- α -ethyl- and β -Phenyl- α -methylpropionic Acids." By ROBERT HOWSON PICKARD and JOSEPH YATES.

A description was given of the resolution of five racemic acids by the fractional crystallisation of their *l*-menthylamine salts. The principal experimental results are recorded in the accompanying table.

133. "The Influence of Hydroxy- and Alkylxy-groups on the Velocity of Saponification." (Part II.). By ALEXANDER FINDLAY and EVELYN MARION HICKMANS.

The velocities of saponification of ethyl glycolate, lactate, α -hydroxy- β -phenylpropionate, γ -hydroxy- γ -phenylbutyrate, phenylpropionate, propionate, β -hydroxy- β -phenylpropionate, and of methyl phenylacetate have been determined. The values of the saponification constant obtained for these esters were 75, 63.5, 40.1, 16.5, 6.9, 5.3, 4.9, 27.4 respectively. From these numbers it is found that

the introduction of a phenyl group accelerates the velocity of saponification, except when the ester contains the hydroxyl group. In this case, introduction of a phenyl group lowers the velocity of saponification (for example, ethyl mandelate and ethyl glycolate). Introduction of an hydroxyl group increases the saponification constant to nearly twelve times its value in the case of esters not containing the phenyl group, but to only five to six times its value in the case of phenylated esters. A comparison of the saponification constants of the ethyl esters with the affinity constants of the corresponding acids shows that there is no general relationship between the two magnitudes.

134. "Apparatus for Experiments at High Temperatures and Pressures, and its Application to the Study of Carbon." (A Correction). By RICHARD THRELFALL.

The author recently described an experiment (*Trans.*, 1908, xciii., 1333) in which graphite was forced through a narrow tube by a comparatively small pressure—negligible in comparison with the pressures under which the property of the fluidity of graphite was employed to transmit pressure. The experiment there described can be repeated as often as desired, but the inference that pressure can be transmitted in all circumstances without any appreciable loss of head by crystalline graphite is wrong. Further experience has shown that when graphite flows it does not obey the laws regulating the flow of liquids, but that the fluidity of graphite is a function of the absolute pressure to which it is exposed. Under high pressures the graphite consolidates, and in this state transmits pressure very badly. For instance, in the experiment described (*loc. cit.*), it is now known that rapid flow took place under a pressure of a few hundred pounds per square inch—the graphite flowing freely into the air. When, however, the graphite, otherwise under similar conditions, was employed to force a pointed piston of hard steel against a soft steel plate, and pressures of 50 to 100 tons per square inch were employed for the purpose, a loss of head of many tons per square inch was found. The observation was made by measuring the depth to which the pointed piston entered the steel plate, and then causing it to penetrate to the same depth by direct pressure. In most of the experiments described in the paper referred to, the graphite flowed into a bath of molten magnesia through a very short neck of unmelted tube, and consequently the experimental results quoted are probably little or not at all affected by the error involved in supposing that graphite, when it flows, obeys the ordinary laws of flow of liquids. Some preliminary experiments indicate that cold lead flowing under high pressure is much more truly a fluid than crystalline graphite.

135. "Experiments on the Constitution of the Aloins." (Part I.). By ROBERT ROBINSON and JOHN LIONEL SIMONSEN.

The authors communicated the results of some further experiments on the nature of rhein, a preliminary note of which has already appeared (*Proc.*, 1909, xxvi., 76).

136. "The Constitution of the Salts of Barbituric Acid." By JOHN KERFOOT WOOD and EMMA ALEXANDER ANDERSON.

The authors have shown that by the action of acetic anhydride on a mixture of carbamide and malonic acid ureidomalonalonamide is formed, together with barbituric acid and an apparently complex substance, the constitution of which has not been established. Ureidomalonalonamide is a white very sparingly soluble substance, which, on treatment with sodium hydroxide, is converted into sodium barbiturate. This action shows that the constitution of the

Dextrorotatory acids.	Acid.					Menthylamine salt.	
	M. p.	[M] _D at 20°.	[M] _D in CHCl_3 .	[M] _D in C_6H_6 .	[M] _D of sodium salt in H_2O .	M. p.	[M] _D in ethyl alcohol.
Δ^8 -Dihydro-2-naphthoic ..	101° (below)	—	+276.2°	+317.0°	+309.0°	143—144°	+251.6
Phenylallylacetic	10°	—	148.9	181.6	40.2	145	—2.7
α -Phenylvaleric	10°	+128.3	104.7	140.7	5.0	141	—58.4
β -Phenyl- α -ethylpropionic ..	10°	—	68.3	73.0	100.7	137	—22.3
β -Phenyl- α -methylpropionic.	10°	37.1	45.5	44.4	66.8	143	+54.6

salts of barbituric acid is represented by the general formula $\text{MO} \cdot \text{C} \begin{smallmatrix} \text{CH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} > \text{NH}$, where M is a univalent metal. Theoretical considerations leading to a similar conclusion were also discussed.

137. "*The Estimation of Carbonates in presence of Nitrites, Sulphides, or Sulphites by means of Potassium Dichromate.*" By ERNEST ROBERT MARLE.

It was proved that soluble carbonates and carbonates of bases which form soluble chromates are quantitatively decomposed by aqueous potassium dichromate. The action of potassium dichromate on nitrites has been investigated. On distillation with dichromate, a nitrite yields nitrous acid, although the mixed solution apparently contains no free nitrous acid. The yield of nitrous acid increases with the concentration of the nitrite, but is almost independent of that of the dichromate.

Prolonged distillation, either adding water at the rate at which the liquid distils, or making the solution up to its original volume after, say, 100 cc. has distilled over, gives 60 to 70 per cent of the nitrite as nitrous acid. The residual nitrite in the flask is estimated, and the loss of 10 to 15 per cent is accounted for by the decomposition of nitrous acid into nitric acid and nitric oxide, some of the nitric oxide remaining dissolved in the dichromate solution.

An apparatus was described with which carbonates can be estimated in the presence of nitrites, the mixture being distilled with dichromate under reflux. The carbon dioxide is thus freed from nitrous acid, and the nitric oxide formed is negligible. The method is found to give accurate results.

SOCIETY OF CHEMICAL INDUSTRY.

Ordinary Meeting, May 3rd, 1909.

Dr. J. LEWKOWITSCH in the Chair.

"*Vulcanisation Tests on Plantation Rubbers.*" By CLAYTON BEADLE and HENRY P. STEVENS.

The work comprises a number of physical and chemical tests made on five samples of rubber before and after vulcanisation. The samples include plantation, block, crepe, and biscuit from young and old trees, and a sample of fine hard para.

Chemical analyses and physical tests were made on the raw rubber, the rubber vulcanised with sulphur only, and also on rubber vulcanised with sulphur and mineral matter.

In addition figures are given for the viscosity of the raw rubbers, and also tests on manufacturers' cut sheet from plantation and fine hard para rubbers.

The authors conclude that the method employed in coagulating and treating the latex has a greater influence on variations in the quality of plantation rubber than a difference in the age of the trees.

"*The Indian Magnesite Industry.*" By H. H. DAINS.

The principal deposits of magnesite lie in the Chalk Hills, two miles from Salem, in the Madras Presidency, South India.

The magnesite covers a superficial area of about 2000 acres, and occurs in abundant irregular veins which percolate an ultra-basic intrusion of eruptive rock called "zunité."

It is only within recent years that much attention has been given to these deposits, but now modern calcining plant for the production of caustic and dead-burnt magnesias has been installed.

The crude and the calcined magnesite are railed 200 miles to Madras by the South Indian Railway, which passes within a mile of the deposits.

It is shipped from there to European ports, where it is used for the manufacture of refractory bricks for basic furnaces, artificial stone, flooring, fireproof partitions, &c.

Generally the magnesite is almost perfectly white. It has a specific gravity of about 3.0—3.06 and a hardness of about 5.

The average mineral is of excellent quality, parcels shipped during 1909 giving 96 to 97 per cent of magnesium carbonate, and being exceptionally low in lime, silica, oxide of iron, and alumina.

"*New Refractometer.*" By J. LEWKOWITSCH.

The author demonstrated a new refractometer constructed by Hans Heele, Berlin, the principle of which is based on the Kuhlrausch-Abbe method of determining the angle at which the limiting ray entering at grazing incidence emerges from a cylinder quadrant made of French flint glass. The details of the construction were suggested by Prof. Harland, of Brussels.

The instrument is so constructed that the angle for air is $34^{\circ} 44' 30''$. The instrument is adapted for all refractive indices from 1.00000 to 1.75632, and can be used for solid as well as for liquid substances and also for gases. The quadrant is surrounded by a water jacket, so that its temperature can be kept constant at any desired degree during the observation.

"*A New Steam Meter.*" By E. A. J. KUHNKE.

The author first discusses the construction and defects of some previous types of steam meter. The new meter described consists of a casing containing a hollow truncated cone of parabolic section, inside which a metal disk is suspended by a wire connected with a counterweight outside the casing. The steam has to pass through the cone. When no steam is passing, the disc closes the upper aperture of the cone; any steam forces down the disc and passes round it. The movement of the disc is directly proportional to the area of the steam passage, and is registered on a clockwork drum, which also records variations of pressure. Tables have been constructed by which the consumption of steam may be calculated from these data, the temperature also requiring to be known in the case of superheated steam. Diagrams exhibiting the mode of use of the meter are shown. The meter is supplied by the Farbenfabriken vorm F. Bayer and Co., who guarantee an accuracy within 3 per cent and a high degree of durability.

FARADAY SOCIETY.

Ordinary Meeting, April 27th, 1909.

Dr. V. H. VELEY, F.R.S., in the Chair.

A PAPER entitled "*Experiments on the Current and Energy Efficiencies of the Finlay Electrolytic Alkali-chlorine Cell.*" By F. G. DONNAN, J. T. BARKER, and P. B. HILL, was read in abstract by Prof. Donnan.

The electrolytic cell referred to was patented in 1906 by Messrs. Archibald and Robert Finlay, of Belfast. It is characterised by the use of a double diaphragm and central brine compartment, whereby the brine solution continuously flows under head from the central compartment through the diaphragm to the anode and cathode compartments, and from these to suitable outlets. By a suitable arrangement of overlapping holes and slots any number of compartments (anodic, cathodic, and brine) and corresponding electrodes can be bolted together. The various compartments are constructed by placing between the diaphragms thin rectangular or square frames of waxed cardboard about 2 to 3 mm. thick. The various layers of electrolyte are therefore simply thin sheets of liquid, so that the electrical resistance per square foot of electrode surface is reduced as much as possible. The anodes consist of rods or slabs of Acheson graphite, the cathodes of sheet-iron. The counter-flow of electrolyte greatly aids in reducing the loss of efficiency caused by electrical migration of the hydroxyl ions towards the anode, and by diffusion and convection of dissolved chlorine to the cathode.

The experiments described in the paper were carried out with small laboratory models suitable for 10 to 20 amperes, and had as their object the determination of the current- and energy-efficiencies of the cell. For this purpose the

asbestos diaphragms sold for electrolytic purposes by Bernfeld, of Leipzig, were employed. It was found that these diaphragms could be used continuously for a month without suffering any serious damage. Purified brine of density 1.18 (about 4.45 normal) was employed in the experiments.

The accompanying table gives an idea of the average results obtained, using as cathode diaphragm a 2 mm. asbestos board, slightly loaded with ferric hydroxide, and as anode diaphragm a 2 mm. (untreated) asbestos diaphragm.

Brine (density = 1.18); Temperature, 17—19°; Current Density = 0.0217 amps./sq. cm.; Average Voltage = 3.37.

Grms. NaOH per 100 grms. cathode liquor.	Per cent current efficiency.	Per cent energy efficiency.	Grms. NaOH per kilowatt- hour.
4	98.0	66.9	434
5	96.5	65.9	428
6	94.5	64.5	419
7	93.0	63.5	412
8	91.0	62.1	403
9	89.0	60.7	394
10	87.5	59.7	388
11	86.5	59.0	383
12	83.5	57.0	370
13	81.5	55.6	361

As regards anodic efficiencies, it was found that when making 7 per cent caustic the anode gases contained 98.4 per cent chlorine, when making 13.6 per cent caustic 94 per cent chlorine. It should be remarked that all the above figures were obtained with anodes of dense amorphous carbon, as at the time of the laboratory tests anodes of Acheson graphite were unfortunately not available.

The experiments show that it is possible with the Finlay cell to make very much stronger alkali at much higher current- and energy-efficiencies than in single diaphragm cells with non-percolating electrolyte. So far as published data go, the results obtained with the Finlay cell appear to be superior to those obtained with the Aussig "bell-jar" process, especially with regard to energy-efficiency. A comparison with the results obtained with the Townsend cell is difficult for want of sufficient data, but it is believed that the Finlay cell would not be likely to suffer from such a comparison.

Mr. ROBERT FINLAY explained that certain disadvantages inherent in the small cell tested by the authors were eliminated in the large units. He believed that in its latest form the cell left little room for further improvement. Solutions containing 8 grms. caustic soda per 100 cc. could now be made at a voltage of 3 from brine at ordinary temperatures, and with a current efficiency of 98 per cent a yield 40 per cent higher than that of the most successful electrolytic process now worked in England. One of the chief features of the cell was the absence of secondary reactions.

Dr. CHARLES J. J. FOX read a paper "*On the Coefficients of Absorption of Nitrogen and Oxygen in Distilled Water and Sea-water, and of Atmospheric Carbonic Acid in Sea-water.*"

The coefficients of absorption of the atmospheric gases in sea-water have acquired some significance of late years, especially in connection with that group of physical problems of which Arrhenius's work on the diathermancy of the atmospheric gases, and especially CO₂ and its effect upon terrestrial temperatures, is typical, and again in connection with the problems concerning the dynamic processes of pelagic life. The best modern determinations (those of Winkler and of Bohr and Bock) of the coefficients for N₂ and O₂ in distilled water are not quite concordant. The apparatus used by the present writer for N₂ and O₂ is a form of the Estreicher Ostwald method, modified and improved for the present purpose. In this modification the pressure can be varied at will, whereas Estreicher had to make the measurements always at exactly atmospheric pressure—a difficult thing to do in practice. Estreicher's

method of freeing the bulb and water from air is also unreliable, and it is suggested that his values for argon may be on this account one-fifth to 5 per cent and the helium values one-half to 10 per cent too low. A very simple method is given for getting over this difficulty of freeing the bulb and water from air.

Two series of measurements of the solubility of atmospheric nitrogen in distilled water between 0° and 50° were made (25 determinations in all). A correction has to be applied, due to the different solubilities of nitrogen and argon and the variation of the partial pressures with temperature, in the experiments. Bohr and Bock's numbers must also be corrected if they are to refer to pure nitrogen, but Winkler's numbers would seem to be correct for pure nitrogen, because they agree very well with the writer's corrected values. When this is done the following numbers are obtained (cc. per litre):—

	0°.	10°.	20°.	30°.	40°.	50°.
Winkler ..	23.48	18.57	15.42	13.40	11.83	10.87
Fox ..	23.00	18.54	15.54	13.55	12.15	11.02
Bohr and Bock	23.20	19.00	15.92	13.38	11.43	10.31

The interpolation formula and values for pure nitrogen are given for every degree from 0 to 50.

Two series of determinations (40 observations) were made also in the case of oxygen between 0 and 50. The interpolation formula and values for each degree are likewise given. Values compared with those of Winkler and Bohr and Bock are as follows:—

	0°.	10°.	20°.	30°.	40°.	50°.
Winkler ..	48.90	38.02	31.02	26.08	23.06	20.90
Fox ..	49.23	38.37	31.44	26.65	23.30	20.95
Bohr and Bock	49.61	39.03	31.71	26.76	23.26	20.70

Determinations were likewise made upon sea-waters of four different salinities (42 observations in all in the case of each gas). These values were then combined with those obtained already for distilled water, and values then calculated for the partial pressures of nitrogen and oxygen in dry air. In the case of nitrogen, the values were calculated to include a constant percentage of 1.185 argon.

In the case of CO₂ the pressure in sea-water varies probably between about 1 to 7 in 10,000, and the total alkalinity also varies, and is for the open ocean equivalent to about 40 mgrms. OH per litre. The CO₂ pressure was determined by Pettenkoffer's method modified for the present purpose. It was first of all established that the ratio of total CO₂ to total OH is rectilinear, and as a consequence of Guldberg and Waage's law no CO₃²⁻ ions are formed, and all of the combined CO₂ must be in the form of HCO₃⁻; this is in conformity with Bodländer's work on the solubility of the less soluble carbonates. This having been established, it was then necessary to determine the effect of varying pressure upon only one alkalinity, that selected being 40 mgrms. per litre. The interpolation formula for CO₂ per litre is in the form $x = pa + yb$. pa is dependent upon the salinity, and the values of it are obtained with sufficient accuracy from Bohr's measurements upon NaCl solutions, and the values are tabulated here for the purpose. These values for pa are about 1 per cent of the total CO₂; yb is the other 99 per cent. A table is given of the most useful values of b for varying temperatures and pressures (1 to 6.5 in 10,000); other values of y are directly proportional to these values.

These tables allow for the first time a calculation to be made of the power of the sea to conserve the constancy of CO₂ in the air, which, since the publication of Arrhenius's papers mentioned above, has become of importance. The conclusion is drawn that for the open ocean (OH = 40 mgrms. per litre and $t = 12^\circ$) it requires 17.6 times as much CO₂ to raise the CO₂ partial pressure as for the same volume of air. Or, since the effective volume of the atmosphere seems to be about eight times that of the ocean, it follows that if a quantity of CO₂ is poured into the air, e.g., by volcanic action, then two-thirds will eventually be dissolved by the sea and one-third retained by the air. But with in-

soluble carbonates on the sea-bottom and CO_2 in the atmosphere above, the sea cannot finally be in equilibrium until either all the one or the other has gone into solution in the form of HCO_3 ; this must take considerable time, though nothing is known about it. But this time factor must be very important geologically.

Finally, the concentration of the free ions HCO_3 and H are calculated. The former is for ocean-water about 2.24×10^{-3} gm.-equivalents per litre, the latter between 1.6 and 2.6×10^{-6} . That is to say, sea-water reacts very nearly neutral *in situ*, and, in fact, just slightly more acid than distilled water. It is in this respect just like blood, and probably all naturally occurring liquids, whether of biological or geological origin, which are not acid initially.

A description of an apparatus used by the writer for extracting and analysing gases dissolved in liquids is also contained in the paper.

Dr. PERCY E. SPIELMANN read a paper "On the Electromotive Force of certain Platinum Compounds, with special reference to the Oxygen-hydrogen Gas Cell."

The author, in association with Prof. R. Lorenz, has investigated the E.M.F.'s of certain platinum hydrated oxides and salts from the point of view of the latter's "oxyd-theorie" for the Grove gas cell.

Part I.—These compounds were measured in a thermostat at 25° against an H_2 electrode by the Poggendorf compensation method for lengths of time varying from a few days to a few months.

The average values obtained are shown in Table I.

TABLE I.

	In N/1 H_2SO_4	In N/1 CH_3COOH	In basic sulphate solution.	In concentrated solution of the respective salts.
$\text{PtO}_2.4\text{H}_2\text{O}$..	—	0.83	—	—
$\text{PtO}_2.3\text{H}_2\text{O}$..	0.98	0.73	—	—
$\text{PtO}_2.2\text{H}_2\text{O}$..	0.96	0.72	—	—
$\text{PtO}_2\text{H}_2\text{O}$..	0.95	0.65	—	—
Basic sulphate	0.91	—	0.94	—
K_2PtCl_6 ..	—	—	—	0.74
PtCl_4 ..	—	—	—	0.94
K_2PtCl_4 ..	—	—	—	0.72
PtCl_2 ..	—	—	—	0.87
BaPtCy_6 ..	—	—	—	0.60

Although the values for the E.M.F. of the hydrated oxides are graded in the direction demanded by theory, their absolute accuracy was doubted when compared with measurements by Streintz of analogous lead compounds. Also there was a possibility of the E.M.F.'s being equalised out by the constant presence of minute traces of impurities and other less likely sources of errors.

Part II.—To obtain the actual E.M.F.'s of the compounds, they were connected to an H_2 electrode and allowed to discharge through a galvanometer. Breaks in the curves indicated the presence of definite substances, many of which were also found by Lorenz and Laube by charging and discharging two platinum plates analogously to lead accumulator plates. These are shown in Table II.

TABLE II.

E.M.F.	E.M.F. of substances, evidence of which was found by Lorenz and Laube.
$\text{PtO}_2.4\text{H}_2\text{O}$..	0.93
$\text{PtO}_2.3\text{H}_2\text{O}$..	0.86
$\text{PtO}_2.2\text{H}_2\text{O}$..	0.74
? ..	0.63
? ..	0.53
$\text{PtO}_2\text{H}_2\text{O}$..	0.45
? ..	0.34
? ..	0.25
? ..	0.15
? ..	0.05

Conclusions.—It is in the highest degree likely that the E.M.F. of the oxygen-hydrogen cell, as usually constructed, is due to a definite hydrated oxide formed by the direct oxidation of the Pt electrode by oxygen in presence of the

electrolyte; this substance, however, has not yet been chemically prepared.

The theoretical value of 1.23 volts can only be reached at temperatures high enough to prevent hydrated oxides from forming, *i.e.*, when a true reversible cell exists.

Also, further evidence is supplied in support of Werner's valency theories, since the N_2O molecules must be closely connected with the structure of the molecule on account of its effect on the E.M.F. of the substance. Grave doubt is thrown on explanations of the decomposition potentials of H_2SO_4 between platinum electrodes.

This paper should be read in conjunction with those of Lorenz and Hauser, and Lorenz and Laube. The original must be consulted for details of apparatus and measurements, and for a considerable amount of evidence quoted to show the comparative ease of oxidation of platinum.

Dr. F. G. DONNAN thought that the compensation method was not inferior to the discharge method. The so-called "oxide" theory was not new.

Dr. G. SENTER referred to the work of Bose, who had charged up platinum electrodes for several days till saturated, and then discharged. He himself, and afterwards Tafel, had shown that platinum dissolved under certain circumstances.

Dr. C. J. J. Fox pointed out that an oxidising substance was produced in the neighbourhood of an oxygen electrode.

Dr. N. T. M. WILSMORE said that the absorption of oxygen by the platinum was probably the cause of the E.M.F. of a gas cell never reaching equilibrium.

Dr. V. H. VELEY remarked that both chemical combination of platinum and oxygen and physical occlusion of the latter had to be taken into consideration.

Dr. SPIELMANN, in reply, said that Prof. Lorenz had worked out thoroughly the "oxide" theory. The compensation method was reliable if pure substances were employed. Bose was not dealing with an OH-cell.

CORRESPONDENCE.

THE ESTIMATION OF TELLURIUM.

To the Editor of the Chemical News.

SIR,—I have just read Gutbier and Flury's contribution to the CHEMICAL NEWS (xcix., p. 217), in which the favourable opinion I expressed six years ago regarding Frerichs's method of gravimetrically estimating tellurium is strongly questioned, and also the statement made that Frerichs has reported to one of these chemists that a new investigation of the process made by himself "bears out the results of Gutbier and Wagenknecht" (*Journ. Prakt. Chem.*, 1902, [2], lxxvi., 261) as to its unreliability. In reply I may state that at the moment I cannot refer to either my original papers or laboratory journals for 1901-2-3, and so am unable to refresh my memory on the subject. However, I promise to re-open the question very soon, and will then deal with Gutbier and Flury's results. Meanwhile, I may mention that I do not share the opinion of these gentlemen as to the impossibility of overcoming the iodine difficulty to which they refer, nor do I consider it impracticable to base a reliable method on the lines involved in Frerichs's original process—Frerichs's correction of himself notwithstanding.—I am, &c.,

R. W. EMERSON MACIVOR.

Metallurgical Laboratories,
1, Phipp Street, Finsbury, E.C.

Aldehyde from Pinene.—C. Harries and Hans von Splawa-Neyman.—When warmed with glacial acetic acid the hydroaromatic ozonide of pinene yields a product by the fractional distillation of which a liquid of an aldehydic nature is obtained. With semicarbazide it gives a disemicarbazone of pinene aldehyde. Theoretically, two trans-isomers of pinene aldehyde, $\text{C}_{10}\text{H}_{16}\text{O}_2$, should exist.—*Berichte*, xlii., No. 5.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlviii., No. 13, March 29, 1909.

Hydrolytic Dissociation of Bismuth Chloride.—Réne Dubrisay.—If the equation $\text{BiCl}_3 + \text{H}_2\text{O} = \text{BiOCl} + 2\text{HCl}$ represents what actually occurs when bismuth chloride is decomposed by water, three independent constituents (Bi , H_2O , and HCl) are present in two distinct phases. Hence at constant pressure the system should be divariant. Moreover, since the reaction sets free 7·830 cal., according to the law of the displacement of equilibrium a rise of temperature should correspond to a decrease in the degree of dissociation. The author has investigated these predictions experimentally, and finds that they are both fulfilled.

Impossibility of Foretelling by Thermochemistry the Relative Stability of Corresponding Compounds of Silver and Lead.—Albert Colson.—The compounds of silver and lead exhibit striking resemblances, but the carbonate and nitrate of lead have much higher heats of formation than the corresponding salts of silver. Hence it might be concluded that they are more stable. This, however, is not the case; for instance, lead nitrate begins to decompose at 283° under a pressure of 20 mm., while silver nitrate does not decompose even at 350° in a vacuum. Thus the heat of formation of similar compounds does not give any information regarding their relative stability, and at constant temperature a definite compound such as lead nitrate may be more stable when dissolved, although its heat of formation is diminished by solution.

Preparation of New Chlorides of Silicon belonging to the Silico-Methane Series.—A. Besson and L. Fournier.—When a dark discharge is passed through a mixture of the vapour of silico-chloroform and hydrogen, compounds SiH_2Cl_2 and SiH_3Cl are not obtained, but a yellow oily liquid condenses. From this liquid the following compounds can be isolated:— SiCl_4 , Si_2Cl_6 , Si_3Cl_8 , $\text{Si}_5\text{Cl}_{12}$, $\text{Si}_6\text{Cl}_{14}$. Finally, after these compounds have been removed by heating, an amorphous solid is left. Its composition corresponds to the formula Si_2Cl_3 , and it is probably a mixture of several chlorides. This method of obtaining chlorides of silicon of the saturated series has the advantage of giving the substance in a very pure state, and containing no oxychloride.

Purification of Hydrated Sulphuric Acid containing Arsenic.—M. Morancé.—When sulphuric acid obtained from the Glover tower is subjected to a temperature of from -8° to 2° for twenty-four hours a portion (rather more than half) solidifies. The impurities present in 100 parts of the monohydrated acid are shown in the following table:—

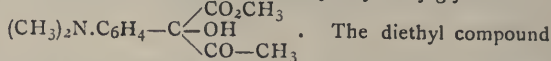
	Solid part (grm.)	Liquid part (grm.).
Residue at a red heat..	0·281	0·829
Iron and aluminium ..	0·029	0·119
Arsenic.. .. .	0·033	0·368

Hence freezing provides a means of purifying sulphuric acid, especially as regards arsenic.

Colouring Properties of Picric Acid.—Léo Vignon.—The colour of picric acid in different solvents varies in the same way as the electrical conductivity of these solutions. Aqueous solutions of picric acid dye wool, and decrease in strength when their conductivity reaches a certain value. This condition may be realised either by increasing the quantity of picric acid in the solution or by adding an acid such as hydrochloric acid to the bath. In alcoholic solution the fixation of the colouring matter is very slight in presence of 1/10,000 of hydrochloric acid in

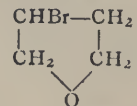
spite of the conductivity. Apparently the fixation of picric acid on wool is due to a chemical reaction of the fibre on the colouring matter strongly ionised in water.

Condensation of Methyl Diketobutyrate with Aromatic Carbides and Amines.—A. Guyot and V. Badonnel.—Methyl diketobutyrate readily condenses with dimethylaniline, the product of the reaction being methyl paradimethylamidophenylacetylglucolate:—

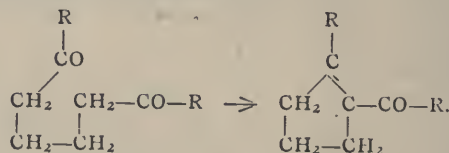


can be prepared similarly. The diketobutyric ethers condense with aromatic carbides in two stages, a phenylacetylglucolic ether, $\text{C}_6\text{H}_5 \cdot \text{C}(\text{OH})(\text{CO} \cdot \text{CH}_3)(\text{CO}_2\text{R})$, being first formed. This then fixes a second molecule of carbide and gives a diphenylacetylacetic ether, $(\text{C}_6\text{H}_5)_2 \cdot \text{C}(\text{CO} \cdot \text{CH}_3)(\text{CO}_2\text{R})$.

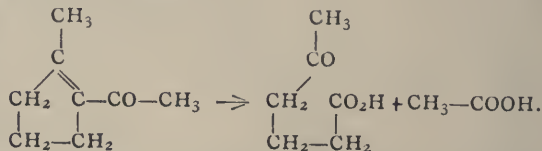
Allylcarbinol. Passage to Furfuran Series.—H. Pariselle.—Allylcarbinol with bromine in chloroform solution gives the dibromide $\text{CH}_2\text{Br} - \text{CHBr} - \text{CH}_2 \cdot \text{CH}_2\text{OH}$. This compound when treated with potash yields the monobromide of tetrahydrofuran—



Cyclisation of Acyclic Diketones.—E. E. Blais and A. Koehler.—The diketones, under the action of alkalis in alcoholic solution, readily yield cyclic compounds, the products being practically pure:—



The composition of the cyclic compound is readily proved by oxidation with permanganate. Thus Perkin's methyl-dihydropentane methyl ketone gives acetic acid and γ -acetylbutyric acid:—



The ζ diketones may be converted into cyclic compounds by the action of concentrated sulphuric acid, but the process is less easy than with the ϵ diketones; cyclic products cannot be obtained from the η diketones.

MEETINGS FOR THE WEEK.

TUESDAY, 25th.—Royal Institution, 3. "The Hittites—(2) Recent Discoveries in Asia Minor and Northern Syria," by Prof. J. Garstang.

WEDNESDAY, 26th.—Royal Society of Arts, 8. "The Manufacture of Nitrate of Soda from Atmospheric Nitrogen," by Sam Eyde.

THURSDAY, 27th.—Royal Institution, 3. "Newfoundland," by John G. Millais, F.Z.S.

— Royal Society of Arts, 8. "The Functions of Schools of Art in India," by Cecil L. Burns.

FRIDAY, 28th.—Royal Institution, 9. "Advances in our Knowledge of Silicon as an Organic Element," by J. Emerson Reynolds, F.R.S., &c.

SATURDAY, 29th.—Royal Institution, 3. "The Secret Societies of the Banks' Islands," by W. H. R. Rivers, F.R.S.

THE CHEMICAL NEWS.

VOL XCIX., No. 2583.

ON THE SODIUM AND THE CHLORINE IN RIVER AND RAIN WATERS.

By H. S. SHELTON, B.Sc.

THE question concerning the quantity of sodium and chlorine in river and rain waters is one that has of late years become of great theoretical importance in connection with geology and with cosmological speculation. One instance of this is found in Prof. Joly's famous paper on the age of the earth as deduced from the quantity of sodium in the sea (*Trans. Roy. Soc. Dublin*, vol. vii., p. 26 et seq.). With the geological side of these questions the present paper is not concerned, but it is evident that all such speculations, whatever value they may otherwise possess, are based on the calculation as to how much sodium actually does enter the sea each year. This depends on the sodium analyses of river waters, which is distinctly a chemical question.

Of this quantity there have been two estimates: one by Prof. Joly based on the statistical results of Sir John Murray (*Scottish Geographical Magazine*, 1887), and a second by M. Dubois (*Proc. Amsterdam Academy*, 1902) based on a careful examination of the more recent river analyses. It is a remarkable and interesting fact that the latter estimate is less than a quarter of the former. The original intention of the present writer was to compile a more accurate series of statistics, but a careful examination of a large number of data was sufficient to show that the average river analysis was not good enough to give a reliable basis for such speculations. It was not possible to correlate the quantity of sodium in the water with the geology of the country or with any known feature, with the possible exception of the personal equation of the analyst.

The following brief calculation will show the order of accuracy required. According to Sir John Murray's data the sodium in the average river water is 3.47 per cent of the total solid (see Clarke's "Data of Geochemistry," p. 88). This, as calculated by Prof. Joly, allowing 10 per cent chlorine for cyclic salt, gives the result of 89 millions of years for geologic time. Assuming cyclic salt to be the more likely number of 90 per cent chlorine, this would thereby become 130 millions of years. If, however, the sodium were 2.47 per cent total solid and 90 per cent of the chlorine cyclic, geologic time would be raised to 225 millions of years. With sodium 1.42 per cent total solid and 90 per cent of the chlorine cyclic, this factor would amount to 2000 millions of years. It will thus be seen that any possible calculation of this kind assumes a very high order of accuracy in sodium analyses.

As an example of the type of analysis on which the calculations are based, the following will show the kind of discrepancy that is exhibited when it is sought to combine these various results by the methods of statistical inquiry.

The analyses in the table refer to the same river, the Mississippi, at the same place, Minneapolis, and are extracted from the same *résumé* (Clarke's "Data of Geochemistry," p. 65).

It will thus be seen that the alkali in analysis 3 works out to double the average of 1 and 2. This particular discrepancy has been chosen because it is not easy to attribute it to any of the causes which usually affect the contents of river waters. They cannot, for example, be put down to sewage, as the chlorine in all cases is small and constant. Nor can the composition be affected by flowing past a large town, because the two which agree so well were taken on either side of the city of Minneapolis. And against the possible suggestion that the discrepancy is due to the artificial pollution of the river by large quantities of gypsum

Percentage of Total Solids.

	1.	2.	3.
CO ₃	55.62	52.76	47.04
SO ₄	1.8	2.04	9.61
Cl	0.91	1.08	0.85
NO ₃	Trace	Trace	—
PO ₄	—	—	—
Ca	23.38	23.9	20.59
Mg	8.24	6.75	7.67
Na	1.77	1.81	5.33
K	0.76	1.28	—
SiO ₂	7.16	9.46	8.01
Al ₂ O ₃	—	—	—
Fe ₂ O ₃	0.36	0.92	0.05
Total solid per million parts by weight	188	177	200

1. Above Minneapolis (Dodge, 1882). 2. Below Minneapolis (Dodge, 1882). 3. At Minneapolis (Barr and Spalding, 1897).

between the years 1882 and 1897, it is only necessary to mention that in another analysis taken in 1884 at Brainerd the amount of sodium is estimated at 5.14 ("Data of Geochemistry," p. 65). The general agreement of the three analyses combined with the unusual difference in the sodium can obviously best be explained by a difference in the method of estimating the latter. For the purposes of river analysis the exact estimation of the sodium, an element which is at the same time a minor constituent, unimportant from the point of view of purity for potable purposes, and one of the most difficult to estimate accurately, is of comparatively small interest and is liable to be overlooked. Nor is there in the statement of the ordinary analysis any means of discovering whether this particular item is a rough estimate or an exact determination.

Another point that is commonly overlooked by water analysts is the bearing of their work on the theoretical question of the origin of the chlorine in the sea. Chlorine is a negligible constituent in all the ordinary igneous and (with the exception of salt beds) sedimentary rocks, and yet it is a universal constituent in river waters. Of the possible sources the following are the most important:—(1) Cyclic salt, (2) hydrochloric acid, and other chloride vapours emitted in the neighbourhood of volcanoes. The importance of separating these varying factors and so indicating the origin of marine chlorine is obvious to those acquainted with these controversies.

One other problem which deserves consideration is the manner in which the cyclic salt reaches the surface of the earth. This has usually been treated as if it depended entirely on the salt contained in rain water. But there appears to be no reason why this deposition should necessarily be associated with rain. In a district of frequent rainfall it is clear that the greater part of such soluble floating matter would come down with the rain; but in dry regions there is no reason to assume that this may not be deposited in the form of dust.

With the view of minimising these varying causes of uncertainty, the author desires to submit the following suggestions to river and rain water analysts, especially to those who live away from the neighbourhood of large towns:—

1. That the river water analyst should always indicate whether his statement of the quantity of alkali, and particularly of sodium, is intended as a rough estimate or as an accurate analysis, and that he should state the degree of accuracy which he thinks belongs to this particular factor. (If this were done, it would prevent the use of data for purposes for which they were not intended).

2. That, where possible and convenient, special care should be taken in the estimation of the sodium, that this should be done directly, and not, as suggested in some books of analysis, by difference (see Wanklyn, "Water Analysis," p. 123). That special care should be taken to observe all the ordinary precautions, such as the use of

platinum vessels for boiling down the water, and of reagents free from all traces of sodium, and that the analyst should state whether the determination has been taken immediately after the water has been procured or whether it has been kept for long periods in glass bottles.

3. That rain water analysts should determine the sodium and the chlorine separately instead of taking the latter as a measure of the former. (This would enable us to discover whether any of the chlorine existed in the form of hydrochloric acid or whether the deposition of this substance in rain water was confined to volcanic regions and to the neighbourhood of large towns).

4. That analysts living in regions of infrequent rainfall should, by exposing a metal vessel to the air, endeavour to ascertain whether any measurable quantity of sea-salt is deposited independent of the rainfall.

It is clear that such experiments as these cannot, without great trouble and expense, be performed by any single worker, but, if they were carried out by those ordinarily engaged in river and rain water analysis, they would make that work of much greater theoretic interest and importance.

It is hoped that these few suggestions may serve the double purpose of preventing geologists from basing cosmic speculation on very insecure foundations, and of suggesting to analysts the great theoretic interest of work which is of minor importance for the more immediate purposes of their analyses.

ANHYDROUS HYDRONITRIC ACID.*

I.—ELECTROLYSIS OF A SOLUTION OF POTASSIUM TRINITRIDE IN HYDRONITRIC ACID.

By A. W. BROWNE and G. E. F. LUNDELL.

It has been shown by several investigators that anhydrous liquid ammonia is incapable of conducting the electric current except to a very limited extent (Cady, *Journ. Phys. Chem.*, 1896, i., 707; Goodwin and Thompson, *Phys. Rev.*, 1899, viii., 38; Frenzel, *Zeit. Elektrochem.*, 1900, vi., 477, 485, 493; Franklin and Kraus, *Am. Chem. Journ.*, 1900, xxiii., 277; *Journ. Am. Chem. Soc.*, 1905, xxvii., 191); that it exhibits remarkable power as a solvent (Gore, *Proc. Roy. Soc.*, 1872, xx., 441; 1873, xxi., 140; Franklin and Kraus, *Am. Chem. Journ.*, 1898, xx., 820), and that its solutions are in general good conductors of the electric current (Cady, *loc. cit.*; Goodwin and Thompson, *loc. cit.*; Franklin and Kraus, *Am. Chem. Journ.*, 1900, xxiii., 277; 1900, xxiv., 83; *Journ. Am. Chem. Soc.*, 1905, xxvii., 191; Franklin and Cady, *Journ. Am. Chem. Soc.*, 1904, xxvi., 499). It has also been shown that anhydrous hydrazine is a poor conductor of the electric current (Cohen and de Bruyn, *Proc. K. Akad. Wetensch.*, Amsterdam, 1903, v., 551; *Journ. Chem. Soc.*, 1903, lxxxiv., [2], 405), that it acts as a solvent toward a number of inorganic salts (Lobry de Bruyn, *Rec. Trav. Chim.*, 1896, xv., 174), and that as an ionising solvent it is comparable with water (Cohen and de Bruyn, *loc. cit.*).

The electrical conductivity of hydronitric acid in aqueous solution has been determined by Ostwald (see Curtius and Radenhausen, *Journ. Prakt. Chem.*, 1891, [2], xliii., 207), by Hantzsch (*Ber.*, 1899, xxxii., 3066), and by West (*Journ. Chem. Soc.*, 1900, lxxvii., 705). Hittorf has investigated the behaviour of ammonium trinitride in aqueous solution toward the electric current (*Zeit. Phys. Chem.*, 1892, x., 593). Peratoner and Oddo (*Gazz. Chim. Ital.*, 1895, xxv., [2], 13; *Chem. Centralbl.*, 1895, ii., 864), have electrolysed solutions of hydronitric acid and of sodium trinitride with a view of investigating the possible formation of polymeric nitrogen (see Note), which they

assumed might be obtained in the form of argon. Szarvasy (*Journ. Chem. Soc.*, 1900, lxxvii., 603), in connection with a study of the behaviour of the various hydrides of nitrogen toward the electric current, has electrolysed solutions of hydronitric acid and of sodium trinitride:—"Slight traces of ammonia but no oxidation products of nitrogen were found in the electrolysed liquid. In some of the experiments the ratio of hydrogen to nitrogen was found to be less than that required by the expression $H_2 : 3N_2$. (That the author intended to make an exactly opposite statement is shown by his next sentence). The deficiency of nitrogen seemed to indicate that some condensation of this element to a polymeride of the type N_3 or N_6 had taken place on the anode during the electrolysis. In order to test this possibility, density determinations of the gas evolved under two sets of conditions were made, but in each case the values obtained proved it to be pure nitrogen." Peratoner and Oddo (*Gazz. Chim. Ital.*, 1900, xxx., [2], 95; *Chem. Centralbl.*, 1900, ii., 660) have expressed the opinion that the deficiency of nitrogen observed in the experiments of Szarvasy might be attributed to the influence of secondary reactions.

(NOTE.—Dennstedt (*Chem. Ztg.*, 1895, xix., 2164; *Chem. Centralbl.*, 1896, i., 191), has also suggested the possible identity of the hypothetical polymer, N_3 , with argon. Dennstedt and Göhlich (*Chem. Ztg.*, 1897, xxi., 876; *Chem. Centralbl.*, 1897, ii., 1093), have attempted to prepare this polymer by the oxidation of hydronitric acid in aqueous solution with potassium permanganate. Compare Dennis and Browne (*Journ. Am. Chem. Soc.*, 1904, xxvi., 607; or *Zeit. Anorg. Chem.*, 1904, xl., 104). Hantzsch (*Ber.*, 1900, xxxiii., 522) has endeavoured to obtain the polymer, $(N_3)_2$, by means of the reaction between silver trinitride and iodine trinitride, as expressed by the equation $AgN_3 + IN_3 = AgI + (N_3)_2$).

In 1891 Curtius and Radenhausen (*loc. cit.*), prepared anhydrous hydronitric acid by dehydration, with calcium chloride, of the 91 per cent acid obtained by repeated fractionation of an aqueous solution of the substance. The anhydrous acid is described as a colourless mobile liquid, which boils without decomposition at 37° , is miscible with water and alcohol, possesses an unbearable odour, explodes violently when brought into contact with a hot object, and sometimes explodes spontaneously even at room temperature. Dennis and Isham (*Journ. Am. Chem. Soc.*, 1907, xxix., 216) prepared anhydrous hydronitric acid by treatment of dry potassium trinitride with sulphuric acid (two parts of acid to one part of water, by volume). The liquid obtained by this method was shown by analysis to contain 99.94 per cent of hydronitric acid. The melting-point of the substance was found to be at -80° . The results obtained in a determination of the vapour density indicate that at 62° hydronitric acid has the molecular formula HN_3 .

From the behaviour of anhydrous ammonia and anhydrous hydrazine toward the electric current, and from the ability of each of these substances to act as an ionising solvent, it seems reasonable to suppose (1) that anhydrous hydronitric acid should show a very low electrical conductivity, (2) that it should possess the power of dissolving numerous substances, and (3) that solutions of inorganic salts in hydronitric acid should be relatively good conductors of the electric current.

In the present article is recorded the first of a series of researches undertaken for the purpose of demonstrating the foregoing statements, of studying the possible formation of the polymer, $(N_3)_2$, and of investigating the chemical behaviour of anhydrous hydronitric acid toward a number of other substances. The work has been undertaken at the suggestion of Prof. Dennis, and is to be regarded as a continuation of the researches of Dennis and Isham (*loc. cit.*).

Preparation of Materials Used in the Experiments.—The hydronitric acid employed in all experiments except the last four was prepared by the Wislicenus method (*Ber.*, 1892, xxv., 2084) as modified by Dennis and Browne

*Reported at the Thirty-eighth General Meeting of the American Chemical Society, held at New Haven, Conn., June 30th to July 2nd, 1908. From the *Journal of the American Chemical Society*, xxxi., No. 4.

(*loc. cit.*). In order to eliminate the possible objection that certain phenomena observed during the experiments might be attributable to the presence of impurities in the acid prepared by this method, the acid used in the last four experiments was prepared by the entirely different hydrogen peroxide method (*Journ. Am. Chem. Soc.*, 1905, xxvii., 551).

The potassium trinitride was invariably allowed to crystallise from an aqueous solution which had been slightly acidified with hydronitric acid (*Journ. Am. Chem. Soc.*, 1898, xx., 225), and the crystals were thoroughly dried *in vacuo* at room temperature.

The anhydrous hydronitric acid was prepared by the method of Dennis and Isham. A weighed amount of the dry potassium trinitride was introduced into a 250 cc. distilling flask. Sulphuric acid (2 : 1) was slowly dropped upon the salt from a separatory funnel, and a slow current of pure dry air was passed through the flask, which was in general partly immersed in water heated to about 40°. The hydrogen trinitride vapour was carried by the current of air from the flask through a glass-stoppered U-tube filled with calcium chloride, into the electrolytic cell, where it was condensed with the aid of liquid air. In one experiment the attempt was made to condense the vapour with the aid of ice. It was found, however, that the greater part of the vapour remained uncondensed, and was carried from the cell by the current of air. This indicates that hydronitric acid has a very appreciable vapour pressure at 0°, and that with the particular form of apparatus employed in these experiments it is necessary to use a much more efficient refrigerant than ice, in order to insure complete condensation of the vapour.

Apparatus Employed in the Experiments.—In designing a suitable electrolytic cell it was found necessary to keep in mind the following desiderata:—(1) the hydronitric acid may be readily condensed and readily distilled off, as occasion requires; (2) the hydronitric acid may be kept at any desired temperature within reasonable limits; (3) the gases liberated during the electrolysis of solutions of potassium trinitride in hydronitric acid may be collected and drawn from the cell; (4) leakage of the poisonous fumes of the acid is prevented; (5) the smallest possible amount of the acid suffices for the work. The desirability of the fifth precaution becomes evident when the explosive character of the acid is borne in mind.

After considerable preliminary experimentation the form of apparatus shown in Fig. 1 was adopted. This consists essentially of the U-tube A (10 cm. high, 1 cm. inner diameter), the left arm of which is provided with a small bulb. Each arm of the U-tube is furnished with a side-tube, s and s', of 4 mm. inner diameter, which slopes in slightly toward the centre. The bottom of the U-tube is made as nearly as possible horizontal except for a slight depression exactly below each arm, which serves the purpose of reducing to the smallest possible amount the necessary quantity of hydronitric acid used. Each arm is carefully fitted with a small cork through which passes a three-way stopcock, c and c', the side-arm of which communicates, through a short capillary elbow-tube, e and e', with a Hempel gas burette, F and F', which is filled with mercury. Sealed to the stopcocks are the graduated and calibrated tubes, B and B', which have a working capacity of about 1 cc. each, and which are of sufficiently small diameter to permit the reading of the meniscus level to within 0.01 cc., with a fair degree of accuracy. Through each of these tubes, which extend nearly to the bottom of the depressions in A, is fused a platinum wire of 0.3 mm. diameter, to the lower end of which is welded a platinum electrode, L and L', 1.0 cm. long and 0.25 cm. wide. From the point at which it is fused into the tube, each of these wires passes upward through the cork to the outside, where connection is made with the rest of the circuit.

A diagrammatic representation of the circuit in which the cell was placed is shown in Fig. 2. The Weston milliammeter used in the experiments is represented by A,

and the voltmeter by V. The voltmeter was never thrown into the circuit for more than a moment at a time, and of course this was never done without cutting out the voltmeter. It was at first hoped that the voltmeter readings would furnish a definite indication either of the formation or of the non-formation of a polymeric form of nitrogen. When it was found, however, that appreciable amounts of ammonia were formed during the electrolysis, it was recognised that the voltmeter could give information of but little value for this purpose, and that reliance must be placed upon direct tests or observations rather than upon the voltmeter readings.

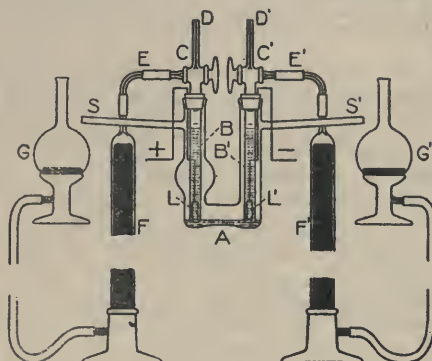


Fig. 1

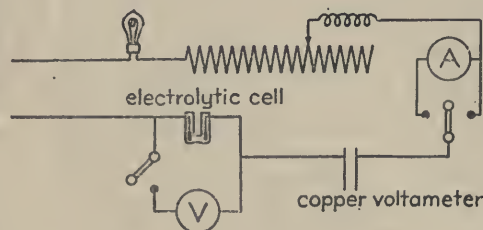


Fig. 2.

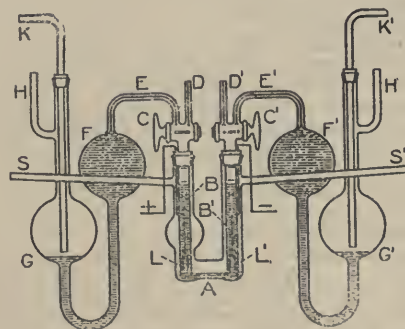


Fig. 3

The apparatus shown in Fig. 3 was constructed with a view of ascertaining whether any indication of the presence of an oxidising agent could be found in the gaseous products of electrolysis at the anode. The gas burettes shown in Fig. 1 are replaced by small gas pipettes, F and F', of 50 cc. capacity, which are joined to the respective stopcock tubes e and e' without the aid of rubber connections. Stopcocks of a different sort are used, to which are sealed, as before, the graduated and calibrated tubes B and B'. The pipettes are filled with a 1 per cent solution of pure potassium iodide. The solution in the anode pipette F is saturated at the outset with nitrogen gas, and that in the

cathode pipette F, with hydrogen gas. To prevent loss of the collected gases in the pipettes by gradual diffusion through the liquids, slow currents of nitrogen and hydrogen are passed through the tubes K and K', respectively, during the course of the experiment. Small test-tubes are inverted over the side-tubes H and H' in order to prevent diffusion of air into G and G'.

In Figs. 1 and 3 it has been found necessary, for the sake of clearness, to represent the U-tube and the calibrated tubes within it as having a diameter nearly twice as large, with reference to their length, and with reference to the dimensions of the other parts of the apparatus, as they had in actual practice. Moreover, in the actual apparatus both stopcocks were in each case turned to the front, so that it was possible to open or to close them from a distance with the aid of a long wooden stick.

In every case the apparatus for the generation of the anhydrous acid was connected to the side-tube S' of the electrolytic cell. To prevent the escape of fumes into the air, the side-tube S was closed by a glass stopcock which was connected on the other side with a chain of absorption bottles containing either an aqueous solution of potassium hydroxide, or, in some experiments, an aqueous or an alcoholic solution of potassium iodide. During the collection of the acid, and during its evaporation at the conclusion of an experiment, the stopcock was left open; during the electrolysis it was kept closed.

In view of the fact that from 2 to 9 grms. of anhydrous hydronitric acid were employed in each experiment, it seemed advisable to adopt unusual precautions to insure the safety of the operators. Two wooden screens, 6 feet high and 3 feet wide, made of 2-inch pine planks, were placed in front of the apparatus. The stopcocks were adjusted with the aid of a long stick which passed through a small hole in the screen, and which was provided with a suitable slot at one end. The electrical instruments were located at a distance of about 15 feet from the cell. By the use of a cathetometer telescope it was found possible to make many of the readings of the gas volumes at some distance from the apparatus. Whenever it became necessary to handle the apparatus, or to stand in its immediate neighbourhood, the eyes of the operator were invariably shielded with goggles made of heavy plate glass, and the hands were protected by heavy gloves. When any unusual risk was taken, the additional precaution of holding a plate-glass screen before the face, or of wearing a sheet-iron mask, was adopted.

Electrical Conductivity of Hydronitric Acid.—It was found by repeated experiments upon different samples of anhydrous hydronitric acid prepared by the methods described in one of the preceding paragraphs, that the acid offers a remarkably high resistance to the passage of the electric current. With a potential difference of about 100 volts between the electrodes, a current of from 0.03 to 0.15 milliampère was obtained at a temperature of 0°. The resistance capacity of the cell shown in Figs. 1 and 3, determined by the Kohlrausch bridge and telephone method, with the aid of a 0.02 N solution of potassium chloride, was 23.55 at 23° (see *Wied. Ann.*, 1898, lxiv., 417; also "Das Leitvermögen der Electrolyte," 1898, p. 1). It was found by experiment that the introduction of small amounts of water, or of dry potassium trinitride, increased the conductivity very greatly. When platinum electrodes were used, without previous treatment with hydrochloric acid to remove the iron, the hydronitric acid soon assumed a brownish red tint, due to the presence of ferric trinitride. The conductivity of the solution obtained in this way was of course considerably higher than that of the pure acid. No accurate measurements of the conductivity of the acid, or of its solutions, have been made during the present investigation. This work is now in progress, however, and will be made the subject of a separate communication in the near future. From the preliminary work already performed it seems reasonable to expect that when rigid precautions shall have been taken to exclude the minutest traces of

moisture, the hydronitric acid will be found to have a specific conductivity of about the same order of magnitude as that of very pure ammonia.

Purposes of the Electrolytic Experiments.—The experiments to be described in the following paragraphs have been conducted primarily for the purposes of (1) determining the ratio in which nitrogen and hydrogen are liberated by the action of the current upon solutions of potassium trinitride in hydronitric acid, and of (2) ascertaining whether any preliminary indication may be obtained, under various conditions, of the formation of the hypothetical polymeric modification of nitrogen, $(N_3)_2$.

If the liberation of nitrogen and hydrogen gas were to take place quantitatively, the ratio of the gases would obviously correspond to the expression $3N_2:H_2$. The formation of a polymeric modification of nitrogen should tend to lower this ratio, whether the polymer proved to be an insoluble gas or a soluble gas or liquid which would remain dissolved in the electrolyte. The formation of either ammonia or hydrazine by reduction of a part of the electrolyte would tend to increase the ratio (W. T. Cooke, *Proc. Chem. Soc.*, 1903, xix., 213). The presence of water would tend to lower the ratio, provided that the oxygen and hydrogen gas were liberated quantitatively. In case part of the oxygen were to appear as ozone, the ratio would of course be still further lowered.

Hydronitric acid and its compounds show in many respects a close analogy with the halogen hydracids, especially hydrochloric acid, and their derivatives. Curtius and Rissom (*Journ. Prakt. Chem.*, 1898, [2], lviii., 306) have pointed out, for example, that from a comparison of the solubility of the alkali trinitrides with that of the alkali halides, the conclusion may be drawn that the nitrine group $(N_3)'$ is to be placed between chlorine and bromine in the halogen series. This arrangement is obviously in harmony with the relationship existing between the atomic weights of the halogens and the formula weight of the nitrine group. From the foregoing analogy, and from the repeated failure of attempts made to identify the nitrine group with argon (Peratoner and Oddo, Dennstedt and Göhlich, *loc. cit.*), it seems reasonable to infer that the hypothetical polymer nitrine, $(N_3)_2$, should be an active oxidising agent rather than an inert substance, that it should be able to liberate iodine from acidified solutions of potassium iodide, and that certain of its physical properties should be in conformity with its intermediate position between chlorine and bromine.

(NOTE.—The credibility of this hypothesis is enhanced by the hitherto unpublished results of certain experiments performed in the laboratory of the Cornell University by Mr. Mortimer J. Brown, in April, 1907. By treating an anhydrous ethereal solution of iodine trinitride, prepared according to the method of Hantzsch (*Ber.*, 1900, xxxiii., 522), with an insufficient amount of metallic sodium to unite with both nitrine and iodine, Mr. Brown found that iodine was liberated, and sodium trinitride was formed. When an excess of sodium was used, the solution at first assumed a reddish tint, owing to the liberation of iodine, but subsequently lost its colour as the iodine combined with the sodium).

By plotting the boiling-points and the melting-points of chlorine and bromine against the atomic weights of these elements, curves may be obtained from which the probable boiling and melting temperatures for nitrine may be read by interpolation. The boiling-point should be located in the neighbourhood of -19.3° , and the melting-point at about -88° . A further reason for the hope that a polymeric form of nitrogen should possess some oxidising power is furnished by the close proximity of nitrogen to oxygen in the periodic arrangement of the elements, from which it might be argued that a polymeric form of nitrogen would be in a sense analogous to ozone.

General Procedure followed in the Electrolytic Experiments.—At the beginning of each experiment a weighed quantity of dry potassium trinitride, more than sufficient for the preparation of a saturated solution, was introduced

through one of the side-tubes, s and s', into the liquefied hydronitric acid. Solution was effected with the aid of a current of dry air. In the experiments during which the electrolytic gases were collected for measurement and analysis, the air present in the tubes B and B' was then forced out through the capillary tubes D and D'. This was accomplished by increasing the pressure in the cell, by means of a current of dry air admitted through one or both of the side-tubes, s and s'. By opening each of the stopcocks, c and c', the hydronitric acid was caused to rise slowly in the tubes. When the meniscus had been permitted to approach the top of each tube as closely as possible without risk of losing part of the liquid, the stopcocks were closed, and the electric current was allowed to pass through the cell until the tubes were partly filled with gas. This gas was then caused to escape through D and D', and the process of filling and emptying the tubes was once more carried out in order to complete the removal of the air. The level of the acid in the tubes was then accurately noted, and after the electrical instruments had been arranged in the circuit, as shown in Fig. 2, the electrolysis was commenced. For the purpose of gaining information concerning the progress of the electrolysis at every stage of the experiment, the current was interrupted, and the gas volumes were read as soon as one of the tubes had been nearly filled with the gas. The stopcocks were then turned so that communication was established between the tubes and the gas burettes or pipettes, which had been previously filled with mercury or with an aqueous solution of potassium iodide, and the gas was carefully forced over into the burettes or pipettes. The level of the acid in the tubes was again noted, the circuit was closed, and the gas was collected and transferred as before. These operations were repeated until the samples of gas collected were of convenient volume for analysis. The progressive readings of the volumes of gas in the graduated tubes were of but little value in indicating the absolute amount of gas evolved, as the gases were invariably saturated with hydronitric acid vapour and were always under slightly reduced pressure. As a means of indicating in a relative way the ratio of nitrogen to hydrogen evolved throughout the entire experiment, however, they were of considerable value. After the conclusion of each experiment, the hydronitric acid was driven from the apparatus by immersing the U-tube in water at a temperature of about 40°, and passing a current of air through the tube. In general the acid was absorbed in a solution of potassium hydroxide, with formation of potassium trinitride, which was recovered, dried, and set aside for use in subsequent experiments. In analysing the samples of gas, use was made of a series of Hempel simple mercury absorption pipettes, each of which contained about 10 cc. of the desired reagent (Hempel-Dennis, "Methods of Gas Analysis," 1902, p. 67). In the analysis of the anode and cathode gases, reagents saturated respectively with nitrogen and with hydrogen were used. The gas was in each case passed first into a pipette containing potassium hydroxide, to remove the hydronitric acid vapour. The volume was then accurately measured in a burette provided with a water jacket, and containing mercury as the confining liquid. The gas was transferred to a pipette containing alkaline pyrogallol solution, and was then returned to the burette for the final measurement. Small amounts of oxygen were uniformly found in both anode and cathode gases. This was no doubt due to the unavoidable leakage of small amounts of air into the apparatus, which resulted during the frequent opening and closing of the stopcocks. Corrections were introduced for these small volumes of air. With the apparatus shown in Fig. 3, the following procedure was necessary in removing the gases for analysis. After the hydronitric acid had been distilled off, the U-tube was removed, and the tubes L and L' were connected in turn with a jacketed Hempel burette filled with mercury. Before the samples of gas were drawn over into the burette, mercury was caused to rise through L and L' into D and D', the tubes K and K' were removed, and water was poured into G and G' until the tubes

H and H' were partly filled. The stopcocks c and c' were finally turned so as to establish communication between F and B and between F' and B' and the gases were drawn over into the burette.

(To be continued)

FURTHER EXPERIMENTS WITH CALCIUM ALLOYS AS REDUCING AGENTS.*

By O. P. WATTS and E. R. SUHM.

At a previous meeting of this Society one of the members made a suggestion to the effect that an account of our failures might prove sometimes quite as helpful as an account of the successful researches usually described; so, although the results hoped for when these experiments were undertaken have not been realised, the methods used may perhaps be of value to others who are experimenting along similar lines.

The present paper is a continuation of one which appeared in vol. xiii. of the *Transactions* of this Society, entitled "The Preparation of Calcium Alloys for Aluminothermic Work." In the few experiments tried at that time the reactions were violent and the yield of metal was small. One of the objects of the experiments about to be described was to suppress this violence of reaction.

Since the heats of oxidation per grm. equivalent of calcium and of magnesium are greater than that of aluminium, and because in some proportions the mixed oxides melt at a lower temperature than pure alumina, it was expected that these alloys would prove more effective reducing agents than aluminium, and it was hoped that by their use it might be possible to obtain fused tungsten and titanium as reduction products.

Aluminium versus Calcium-magnesium-aluminium Alloys as Reducing Agents.

At the outset a direct comparison was made between aluminium and an alloy consisting of 30 per cent calcium, 20 per cent magnesium, 50 per cent aluminium in the reduction of a mixture of rutile and manganese dioxide in proportions calculated to yield a manganese-titanium alloy containing 35 per cent of the latter. Charges of 250 grms. were fired in the usual way by magnesium ribbon surrounded by an igniter of barium peroxide and finely powdered aluminium. The granulated aluminium gave an excellent reduction and a good ingot of manganese-titanium alloy, but the reaction of the calcium alloy was very violent, blowing part of the charge from the crucible, and the resulting alloy was scattered through the slag in globules about the size of peas.

Substitution of External Heat for that produced by the Reduction of Manganese Dioxide in the previous Experiments.

Experiment 10.—A charge of 90 grms. pulverised rutile and 81 grms. of the calcium alloy previously mentioned, without the igniter, was heated in a graphite crucible for twenty minutes in a resistor furnace, using 20 kw. The reaction was quiet, but the yield was only 26 grms., or 48 per cent of metal in scattered globules. The temperature had not been high enough for a good separation of metal and slag.

Experiment 11.—The experiment was repeated on a larger scale, heating for ten minutes by 24 kw. a charge of 281 grms. of rutile and 255 grms. of alloy. Twenty-seven grms. of metal were obtained in globules, but much metal was scattered throughout the slag in particles too small for collection. Analysis of the product gave 75.3 per cent titanium and 25 per cent aluminium. This indicated that more than the theoretical amount of rutile is required in

* A Paper read at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 6 to 8, 1909.

the charge in order to completely oxidise the aluminium, and accordingly more than the theoretical proportion of rutile was used in later experiments.

Experiment 13.—245 grms. of alloy were mixed with an amount of rutile 40 per cent in excess of that required by theory, and the charge heated by 17.5 kw. for fifteen minutes. The resulting metal was scattered all through the slag.

Experiment 14.—As a comparison, the same weight of rutile mixed with an amount of comminuted aluminium chemically equivalent to the alloy previously used, was heated by 19 kw. for thirty minutes. There was no outward manifestation of reaction, but reduction had occurred. The metal settled through the slag, and collected in several large globules. This reduction by aluminium was more satisfactory than similar ones in which calcium alloys were used.

Experiment 15.—In the hope of attaining a higher temperature, an alloy consisting of 60 per cent calcium and 40 per cent magnesium was tried upon excess of rutile. The reaction was quiet, although flames came from the crucible for thirty seconds. There was no separation of metal and slag.

It was evident that some way must be found of heating the charge considerably above the temperature at which reaction begins in order that the heat added by the reaction should produce a fluid slag and a good separation of metal. An attempt to add the charge to a crucible previously heated to whiteness resulted in the ignition of the charge before it got inside the crucible, and the consequent burning of the product in the air.

In this juncture an article read a dozen years ago upon the effect of size and shape of grain upon the rate of combustion of the brown prismatic powder used in large ordnance suggested a possible solution. As a result of experiments with grains of various sizes and shapes, and with perforations to increase the amount of surface, it was determined that the combustion of gunpowder is purely a surface phenomenon, and that the rate of combustion depends on the ratio of surface to mass.

In the previous paper upon calcium alloys the violence of reaction was ascribed to the sudden vaporisation of a part of the calcium or magnesium before it could combine with the oxide which was being reduced. Attempts to use more finely pulverised materials and to secure more intimate contact between alloy and oxide had resulted in the blowing of most of the material out of the crucible. The use of briquettes promised to give a fairly slow reaction, even though the reducing agent and oxide were used in a very fine state of division.

The Use of Briquetted Charges to Diminish the Speed of Reaction.

An alloy consisting of 23 per cent aluminium, 35 per cent calcium, and 42 per cent magnesium was ground as fine as possible in a disc pulveriser, mixed with pulverised rutile, and made into briquettes, using a 10 per cent solution of gum-arabic in water as a binding material. The briquettes contained 10 per cent of rutile in excess of the theoretical amount.

Experiment 17.—A crucible of Acheson graphite with an electrically baked lining of magnesia was heated to whiteness in the resistor furnace and the briquettes added one at a time. They slowly settled in the crucible, but gave no other indication of reaction. As a result of this experiment there was on the bottom of the crucible a layer of very porous yellowish metal, with slag above it, then another layer of metal. Near the top the briquettes could still be distinguished, each having a metallic core with slag on the outside.

The briquettes had proved satisfactory in suppressing the violence of reaction, but the temperature attained was still too low for a good separation of metal from slag.

Experiment 20.—A similar experiment was tried using an alloy of the formula Al_2CaMg with the theoretical proportion of rutile. As binding materials solutions of gum

damar, tragacanth, shellac, and linseed oil were used. Graphite crucibles with magnesia linings were heated by 24 kw. for two hours before adding the briquettes. Reaction was quiet in each case. The briquettes made with gum damar gave sparks and some smoke, and those made with linseed oil gave off a thick black smoke for nearly a minute. The result was about the same as in Experiment 17.

An attempt was now made to secure a higher temperature by adding to the charge a considerable excess of calcium alloy and enough barium peroxide to oxidise it, thus adding greatly to the heat of reaction, yet introducing no other metal into the product, as was done when manganese dioxide was used as the oxidising agent. Briquettes were accordingly made of the alloy Al_2CaMg with 10 per cent excess of rutile, to which different amounts of the heat-producing mixtures of alloy and barium peroxide were added.

- | | |
|-----|---|
| (a) | 60 per cent charge and 40 per cent heating mixture. |
| (b) | 50 " " 50 " " |
| (c) | 40 " " 50 " " |

Experiment 21.—A graphite crucible four inches in diameter and six inches high with a magnesia lining was heated to whiteness in the resistor furnace, and the briquettes were dropped in one at a time. All reactions were violent, increasingly so in proportion to the amount of fuel and oxidiser added to the charge. The product was a white porous metal of rather high density, but poorly separated from the slag.

An attempt was now made to obtain fused tungsten by the use of the same alloy as a reducing agent.

Experiment 22.—Briquettes were made of Al_2CaMg and WO_3 , using 15 per cent of the latter in excess of the theoretical amount to insure complete oxidation of the reducing agents. Two charges were made into briquettes, using shellac as a binder.

- | | |
|-----|---|
| (a) | 171 grms. WO_3 + 51 grms. alloy. |
| (b) | 103 grms. of (a) + 103 grms. of BaO_2 and alloy. |

Two graphite crucibles with magnesia linings were heated to intense whiteness by 50 kw. At the end of forty-five minutes heating the briquettes were dropped in.

(a) The reaction was rapid, but not violent, and resulted in a single mass of tungsten. The metal had sintered rather than fused, and was a mere shell, having the form and nearly the size of the original briquettes. The metal was entirely free from slag.

(b) The reaction was very violent, and much material was projected from the crucible. The product was a porous mass of intermingled metal and slag at the bottom of the crucible. The magnesia linings were in good condition.

Experiment 23.—An arc at 40 to 50 kw. was substituted for the resistor furnace in the hope of getting a higher temperature. Briquettes were made with shellac of 297 grms. rutile and 172 grms. Al_2CaMg . A graphite crucible 4 inches in diameter and 6 inches high was placed upon a slab of graphite, which served as one terminal, and surrounded by finely pulverised carbon. The bottom of the crucible was covered with a layer of magnesia to prevent contact of the reduced metal with carbon. The arc was started by laying a small carbon rod on top of the magnesia and bringing the upper electrode down upon it. Pure alumina was added and thoroughly fused. When the current was interrupted for the purpose of adding the charge, the alumina at once solidified. To prevent this, barium carbonate and lime were added, and the whole fused by the arc. The circuit was then broken and briquettes fed in until the slag began to freeze, when the arc was started again, and so on until all the charge had been added. On examining the crucible a few globules of metal were found resting on the magnesia bottom and well separated from the slag above. Half way up was a mixed mass of metal and slag, and near the top was a porous reddish mass that appeared to be titanium nitride, with a thin layer of slag above it. The only good separation of metal and slag occurred at the outset when the

original fusible slag was in large amount compared to the charge.

Adding the Charge to a Fused Slag.

In the hope of getting a better separation of metal a mixture of oxides was fused in the crucible, and the charge dropped into the molten mass.

Experiment 24.—Two Acheson graphite crucibles 4 inches by 6 inches with an inch of magnesia in the bottom were heated in the resistor furnace. 3400 grms. of a mixture having the composition $2\text{CaO} \cdot \text{BaCO}_3 \cdot 2\text{Al}_2\text{O}_3$ was prepared.

(a) The charge was composed of 65 parts of the mixed oxides to 35 parts rutile. When this was thoroughly fused, 100 grms. of aluminium wire in a single piece one-eighth inch in diameter was slowly introduced into the crucible. There was a very marked increase in temperature, and at times the slag boiled over the edge of the crucible. A thin layer of whitish metal was found at the bottom of the crucible. Its colour would indicate that it contained aluminium alloyed with the titanium.

(b) $2\text{CaO} \cdot \text{BaCO}_3 \cdot 2\text{Al}_2\text{O}_3$ was fused, and briquettes of 559 grms. $\text{WO}_3 + 149$ grms. Al_2CaMg were thrust into the fused mass. The reaction was violent, spattering fused slag several feet out of the furnace. There was no separation of metal. The product was dark grey and of high density.

Experiment 25.—The reduction of rutile was tried on a larger scale. 1200 grms. of $2\text{CaO} \cdot \text{BaCO}_3 \cdot 2\text{Al}_2\text{O}_3$ was mixed with 800 grms. of rutile and fused in the resistor furnace. 450 grms. of aluminium wire were then added. After cooling, it was found that the layer of magnesia, placed on the bottom of the crucible at the outset, had disappeared. A layer of titanium on the bottom had taken up carbon from the crucible. Higher up in the crucible there was a considerable mass of white metal, which was found to consist of 80 per cent titanium and 20 per cent aluminium. This method fails to produce pure titanium because of the latter's affinity for aluminium.

Experiment 26.—It is well known that the oxides of tungsten and molybdenum are volatile at high temperatures. This experiment was tried to see if the vaporisation of MoO_2 could not be prevented by causing it to combine with other oxides before the highest temperature was attained. Accordingly, 200 grms. of MoO_2 was mixed with 1200 grms. of $2\text{CaO} \cdot \text{BaCO}_3 \cdot 2\text{Al}_2\text{O}_3$, and the mass fused in a graphite crucible in the resistor furnace. No vaporisation occurred. 600 grms. more of MoO_2 , which is 150 grms. in excess of the aluminium added later, was mixed with the oxides of calcium, aluminium, &c., and gradually added to the fused mass in the crucible. Much vaporisation occurred. Before all of this mixture had been added aluminium wire was fed in, then more mixture, and so on alternately until the whole 182 grms. of aluminium had been added. On opening the crucible, 248 grms. of a white dense metal with a conchoidal fracture was found on the bottom of the crucible. The layer of magnesia which was placed in the crucible had disappeared. Above the metal was a layer of crystalline slag. The separation of metal and slag was perfect. The yield of metal was 51 per cent of theory. A quantitative determination gave 99.5 per cent of molybdenum. This experiment would seem to show that loss of MoO_2 and WO_3 by vaporisation can be prevented by admixture with other oxides, provided the entire charge be put into the cold crucible and heated gradually.

Several additional experiments were tried in the direct comparison of the efficiency of aluminium and Al_2CaMg upon Mn_3O_4 according to the regular Goldschmidt method.

Experiment 27.—(a) 64 grms. $\text{Mn}_3\text{O}_4 + 26.4$ grms. alloy gave an excellent separation of metal from slag, and a yield of 43.4 per cent of the theoretical amount of metal. The reaction was steady and quiet.

(b) 74 grms. $\text{Mn}_3\text{O}_4 + 25.4$ grms. granulated aluminium gave a slow quiet reaction, but a very poor separation of metal from slag.

(c) 256 grms. $\text{Mn}_3\text{O}_4 + 105.6$ grms. alloy reacted quietly, and yielded 70 grms. of metal in a single ingot, a yield of

57 per cent. The metal was hard, dense, and resembled commercial manganese produced by the Goldschmidt process. The slag was greenish in colour, showing a desirable amount of unreduced manganese oxide.

Experiments with Cr_2O_3 on a similar scale yielded only scattered globules of metal. This result is not surprising in view of the statement by L. Guillet ("Les Alliages Metalliques," p. 18), as a result of many experiments, that the reduction of Cr_2O_3 by aluminium is not successful in small charges up to 3 kilograms.

Summary.

The direct comparison of aluminium with the alloys as reducing agents gave conflicting results. In the reduction of a mixture of MnO_2 and TiO_2 aluminium was superior, while in reducing Mn_3O_4 the alloy gave far better results. It is probable that the alloys are superior in all cases where none of the charge is blown out of the crucible. The alloys are distinctly superior to aluminium for the igniting mixture.

Attempts were made to supply enough heat to secure solid masses of tungsten and titanium.

(a) By rapidly heating a charged crucible in a resistance furnace.

(b) By heating with an arc of 50 to 60 kw.

(c) By feeding the charge into a mass of melted oxides.

(d) By adding BaO_2 and extra alloy to the charge.

All these methods failed.

Moulding a charge of very finely pulverised material into briquettes was very effective in suppressing too great violence of reaction.

The vaporisation of MoO_2 can be prevented by getting it into combination with other oxides before an extremely high temperature is attained.

Since the violence of reaction of the alloys increases with the amounts of calcium and magnesium, the most serviceable, as well as the cheapest, alloys will probably be those with only enough calcium or magnesium to be readily pulverised.

LABORATORY ORGANISATION.*

By Professor C. BASKERVILLE.

PROBLEMS incident to a complete reorganisation of a growing department, construction and equipment of a laboratory with adequate provision for a thousand students, and the laying out of suitable courses of instruction for a college proper, have so engrossed my time during the past two or three years, that I have had to forego in a large part the pleasure of the pursuit of research in my special field of inorganic chemistry and offering the results for your consideration. Such is the price the teacher who loves his work must and does pay. As the coming half year promises a consummation of the work in this direction to a fair degree, and as it is the purpose of the authorities of the college to formally dedicate the new buildings in May next, to which ceremony it will be our pleasure in due time to request your attendance, it has appeared appropriate, in preparation for your visit, to present to you this evening and at the two succeeding meetings of the section, a series of three short papers under the titles "Laboratory Organisation," "Principles of Laboratory Construction," and "Courses in Chemistry for Colleges." That such hackneyed titles offer little that is attractive is recognised, yet I am constrained to believe that what I shall have to say will serve as an incentive for discussion. In this connection allow me to remind you of the fact that the institution to which I shall refer more particularly belongs to you, to me, to every man, woman, or child in this great city, who pays taxes or rent. I am merely one of the instruments for making it most effective. Having

* Read before the New York Section of the American Chemical Society. Reprinted from *Science*, N.S., vol. xxviii., No. 696.

centralised my efforts, for the time at least, upon it, I shall welcome every suggestion by which the ideal may be more nearly approached. Human nature prompts a desire for helpful advice and sympathetic criticism. I may add, what is presented this evening will likely provoke an amused smile on the part of those who are associated with large well-organised corporations.

Every department of an educational institution requires some form of organisation. A chemical department is more acutely affected by lack of organisation than any other of the various subdivisions of an educational plant. The nature of the work classes a chemical laboratory under the head of department stores. Every chemical department has some style of organisation. Much consideration of the subject has resulted in settling upon the plan here outlined as most suitable to an institution as the College of the City of New York, which is of collegiate grade only, not offering graduate or technical courses of study. Perhaps with slight variations parts of the plan may commend themselves to other institutions.

The pedagogic phase of the subject, first in importance, is to be considered as the last of the three topics. The material arrangements for securing the best results will be taken up next time. This evening I desire to direct your attention to the consideration of the executive phase, which involves the selection of a staff, the proper care for a large plant, its upkeep and control over current expenses, whereby the largest output and the greatest use may result with the least expenditure.

Complaint is frequently made in this country on the part of directors of laboratories and teachers of chemistry, that they are overcome with detail work. This complaint is, as a rule, well founded, but it is my belief that a system of organisation can be adopted which will relieve the directors of much of the detail work, subdividing it in such a manner that it does not become too great a burden for any one individual.

Clerical Help.

In the first place it is uneconomical to require the head of the department to do much of the clerical work, which may be done by one who has not had to spend so much time in preparation for the duties of a directorship. In short, fuller return is made to the institution by the employment of a clerk or secretary, or both.

Selection of a Staff.

As the head is held responsible for the department, his advice in the selection of subordinates should carry great weight. This is a principle generally recognised in all reputable institutions of learning, although not always lived up to. Many factors are involved in the selection of a staff. I shall limit myself in this connection to two pertinent remarks. Naturally we know our own graduates better than those who come from other institutions and whom we have met incidentally. Our own graduates are more familiar with the local problems, and it is easier to meet the difficulties with sympathetic help. In not a few institutions, however, in-breeding has resulted, if not in stagnation, at least in bringing about a state of affairs which has prevented the department from producing its best results. It is desirable, therefore, to hold enough of the men who know the inside life of the institution to preserve its traditions, yet new blood should be brought in continually to show the best of other places and act as a stimulus for the whole. Withal it is better to have a man two years whom other people want, than to have a man twenty years whom nobody wants.

Time for Research.

It does not follow that the investigator is the best teacher, but a man of research at least has had a taste of the sweets of discovering the unknown, and consequently, with rare exceptions, is more capable of imparting some of that spirit to students than he who knows nothing of such experience. Research must be the prime means by

which the young teacher can hope to attract such attention as may bring him preferment elsewhere. Yet he may not be wanted elsewhere if he neglects the work at hand, namely, his teaching.

The controlling powers are often unfair to the young men who occupy the inferior positions in placing heavy teaching burdens upon them. Time for research, for by it advancement is hoped, is secured often only at the sacrifice of hours of needed rest and recreation, or by neglect of the little but important things of their teaching. I regard it really better business, if I may assume to speak from that point of view, to require less teaching hours for these young men, and to assign them certain times to be used for research, which may or may not be in co-operation with a colleague. (We have provided one room where twelve tutors may have each a private place. Ten private laboratories are provided for those of higher grade). The freshness and vigour of his instruction will be improved and the responsibility for advancement will in a greater degree rest upon the man himself. A staff of ambitious young men secured under the same title and compensation gives an opportunity for competition for preference.

Staff Assignments.

When a staff, or a nucleus of a staff, has been secured, it is advisable to organise the department into divisions. The extent of the subdivision and the duties assigned to the chief of each division will depend upon the number of men available and their qualifications. We have found it convenient so far to divide our department into divisions of general, analytical, organic, and physical chemistry, and supplies. Each chief is held responsible not only for the instruction in his division, all details of equipment, &c., going first to him also, but for certain other matters, for example, the chief of the analytical division has general superintendence of the upkeep of the department; the chief of the physical division supervises the electrical equipment; the chief of the organic division oversees the museum and library, &c. A weekly conference of the whole staff gives an opportunity for suggestions and their discussion.

Control of Numbers.

In a separate building given to any one subject in the curriculum of a college, there must be a fairly large assemblage of students at some time or other, particularly when a portion of the instruction is given by lectures to several hundred at once. Not only must the building be so constructed, but the organisation so effected, that there may be rapid assembly and quick dispersion of people. Counter currents of the throng are avoided by having one stairway for going up and another for descending. Inevitable friction in the passages caused by discharging several groups of students into the corridors at once is avoided by a little foresight in arranging the schedule of recitations and laboratory practice. After three o'clock in the afternoon, after which hour no new class now begins, or in times of emergency, all means of exit are used. They are so arranged that there is no converging of currents, the upstairs leading out one way, and the downstairs leading another. The exemplary conduct of the children in our public schools of New York at times of alarms of fire have often demonstrated the wisdom of such precautions.

Students' Supplies.

The problem of supplies is an ever vexing one with every chemical department. The College of the City is unique in requiring no fees, and by law we must provide sufficient apparatus and chemicals for each student to complete a first-class course in chemistry without cost to him. The cost for the average student, therefore, must be determined for each course. The student has that amount, in terms of supplies, to his credit upon which he may draft as his requirements arise. At the point of overdrawing on the part of an extravagant or careless student, his credit ceases and he must make good any excesses,

Card Catalogue System.

Satisfactory bookkeeping is therefore a necessity. We have adopted the card catalogue system. The system for the division of supplies, including four auxiliary supply rooms, provides requisitions for immediate or temporary use, import orders, desk equipment, and private laboratories; shipping instructions, inventory, labels, tags, &c.

A budget is prepared. The amount of the appropriation is known to the director. All requisitions are recorded with the estimated cost opposite in one column. When the bill for that particular requisition is presented the actual expenditure is placed in an adjoining column. By this means we live within our means, whether they be meagre or extravagant. The Board of Estimate usually avoids the latter, even if we were inclined to extravagance.

The executive side of the system cares for students' registrations, division registration, advancement, admission to advanced standing, record cards, requests for permit to work out of hours, notices of poor work and regular students' reports, &c. The cards are coloured, which facilitates classification, as yellow for analytical, red for organic, &c. The selection of any designating colour once decided upon is adhered to. (Samples of the cards in use were exhibited. They may be had on request to the author).

In elaborating this system I have received hearty aid from my colleagues, Associate Professor H. R. Moody in particular.

Placing Responsibility on the Staff.

The use of a time stamp to indicate the receipt of invoices, date of approval of bills, for stamping of notebooks, &c., has proved of great value in our department in serving to place the responsibilities. In this connection it may be stated in anticipation of a subsequent discussion of certain pedagogic problems that we have the "section system" for laboratory instruction. We do not have large laboratories, but small ones, accommodating, as a rule, not more than twenty-five students at one time. The reason for this will be discussed in a later communication. The instruction in each laboratory is given by one instructor. He is held absolutely responsible for the conduct of that room, including its physical condition. Instructors are human, and when the responsibility is divided, one usually bears the brunt of the work, and the filthy condition of a laboratory is always attributed to the "other fellow." This is a principle and one of fundamental importance. Its application discloses the slipshod clock-watcher, while it rewards the earnest and worthy.

Uniform Reagents.

To bring about uniformity in the use of chemicals throughout the laboratory, where it is possible, reagents are made up in bulk according to a standard, which has a normal basis. These reagents, on requisition to the main stores, are distributed in proper vessels and charged to the respective laboratories to which they are issued. As the instruction in one laboratory is as a rule limited to a particular kind, and as several laboratories are carrying on the same kind of instruction, it is comparatively easy at the end of the semester to determine the consideration given to economy by the instructor in charge. Parsimony may not be a desirable quality in a man, but economy is not a bad habit.

Reagent Bottles.

The missing reagent bottle has been the source of unending worry to instructors and the cause for much useless delay to the student in his work. When the number of reagent bottles goes beyond ten thousand, the problem is serious and the exasperation resulting is likely to be beyond words. It may be solved in large part by burning numbers indicating the floor, room, and desk in with the label. The number of the stopper and bottle is cut by a diamond or etched. A glance shows the completeness of a set of reagents or the location of a misplaced bottle, for bottles will be misplaced as long as human beings use laboratories.

There is only one system which will prevent that, and it is not allowed by the law. I mean the shotgun system.

Lock System.

In order to hold a student responsible for the apparatus with which he is charged, he must be provided with locked cupboards and drawers. These in some laboratories have combination locks. They get out of order and are wasteful of the instructor's time in the semestral cleaning up and refitting. Therefore, we adopted the separate key system, the instructor being supplied with a master-key. To avoid the frequent excuse of leaving keys at home, they are kept upon numbered hooks within a cupboard, provided with a clear glass front, next the bulletin board, which is conveniently placed in each laboratory by the entrance door. The cupboard is opened only by the instructor's master-key. A glance indicates absences and prevents the use of the laboratory by students out of hours without a special permit.

The key system adopted for the entire department may be of interest. The stockroom system (six rooms) are under one key. Each stock-keeper has one. All students' laboratories, lecture and quiz rooms, the key cupboards, students' desks, toilets, janitor's closets, switch boxes for lighting, library, and doors to the building are opened by one master-key. Each member of the staff has one of these. The toilets, janitor's closets, and laboratories are under one key for the cleaners. The suite of executive rooms, including the private laboratory of the director, is under one key. The director's secretary, private and lecture assistants have one. Each private laboratory is under a separate key, that of the chief of the division of physical chemistry controlling the switchboard, storage battery, and electric furnace rooms. The director is provided with a grand master-key which opens every lock in the building except the private desk of each member of the staff.

Electric Current System.

In pursuing the pedagogic policy to which reference has been made, it is necessary to provide students with electric current from storage batteries. These delicate sources of energy require systematic and intelligent supervision. The instructor in charge of a particular laboratory makes requisition upon the chief of the division of physical chemistry for current of definite voltage and an outside limit of amperage. The cells are connected with plugs carrying fuses with the limit of amperage wanted. A careful record of the condition of the cells, when put in service and when disconnected, is made. Communication among the offices, private laboratories (for a staff of thirty), stock rooms, preparation rooms, &c., is facilitated by an intercommunicating telephone system, whereby eight different conversations may be carried on simultaneously and without interference.

Semi-annual Cleaning Up.

The semi-annual cleaning of movable ironware like files, tripods, &c., may best be accomplished by dumping the pieces into an electrolytic tank containing water to which salt has been added. After the passage of the current for a few minutes, the cleaned metal is washed with tap-water and placed in a drying oven. Those articles requiring painting are then dipped in a tank of acid-proof paint and allowed to drain on an incline which leads the excess of paint back to the tank.

Control of Platinum.

We have found it advisable to mark all our platinum ware by a special stamp and register it with each dealer in platinum with the request that any of that metal bearing the "Sign" presented for sale without an accompanying letter of the director, be held pending communication with the department. We have met with gratifying co-operation on the part of the dealers.

Fire Precautions.

It goes without saying that precautionary measures must be taken against the inevitable fires often recurring in laboratories. In each laboratory, depending upon the size of the room, we decided to place tube powder fire extinguishers. The larger rooms have a tube at each end. In the corridors on each floor and in the organic laboratory is an improved Babcock machine. That failing, recourse is had to the fire hose conveniently placed. Each laboratory is connected directly by enunciator bells with the office of the assistant to the director, who is chief of the division of supplies and *ex-officio* chief of our voluntary fire brigade.

In the event that an accident has resulted in setting fire to an individual, recourse is had to the shower which extends over the exit door of each laboratory for students, and the fire-proof blanket hung near by. Emergency medical closets are in the corridors of each floor. An accurate detailed statement of each accident, however small, is filed with the director by the responsible instructor within twenty-four hours. These records are kept open for court or medical inspection.

By the system outlined the head professor secures some time for service on many important committees involving general problems concerning the welfare of the institution. The division of labour has not resulted in any complaints about having placed too heavy a burden upon any one of my associates. Each member of the staff not only earns his salary legitimately, but secures some hours for investigation. The city gets a constant rich return for the investment, for the service is not only good, but fuller, when the work of the individual is stimulated by a happy ambition.

PROCEEDINGS OF SOCIETIES.

RÖNTGEN SOCIETY.

THERE has just been permanently housed at South Kensington, in the western galleries of the Victoria and Albert Museum, a collection of some sixty historical X-ray tubes, which have been gathered together by the Röntgen Society from various sources, British and German. The early Crookes tubes, presented by their designer, are in evidence, as well as the earliest forms of tubes made in England from Röntgen's description, the focus-tubes of Prof. Jackson, and the Muller tube, which received the gold medal of the Röntgen Society in the competition for the tube of best radiographic definition held in 1901. There are tubes specially designed for radiography, for therapeutic work, and for purely experimental purposes. Dr. G. H. Rodman, who has been entrusted with the task of making a photographic record of these specimens, gave a paper on the subject at the meeting of the Society on May 6th.

Mr. J. H. GARDINER also read a paper in the form of an appendix to his lecture before the Society a month ago, which was reported in the CHEMICAL NEWS (xcix., p. 189). His paper was an answer to the criticisms made upon his suggestion that the life of an X-ray tube might be prolonged by attaching a small magnet outside the tube close to the edge of the cathode, so that when one spot on the anti-cathode surface became fused the focus could be deflected to fall on a new place and the tube used again. Since reading the former paper, Mr. Gardiner has been making some further experiments to discover whether such a course of procedure would destroy the radiographic definition. After taking all kinds of precautions, which cannot be detailed in a brief report, he exposed upon a delicately perforated screen of iron three times, once with the cathode focus at its normal place, and the second and third time with the focus displaced by two or three millimetres on

either side of the normal focus. On development the three images were absolutely identical in sharpness, the definition being equally good whether the cathode focus fell naturally upon the anti-cathode or was displaced by the magnet to one or the other side.

At the same meeting, Mr. G. W. RAFFETY showed an experimental tube in which a platinum-faced anti-cathode was hinged to one of aluminium so that it could be moved out of the way of the cathode stream, the purpose being to obtain some comparative results between anti-cathodes of different metals, all other conditions being identical. The paper indicated possible lines of research rather than gave the results of any completed investigation, but Mr. Raffety said that the material of which the anti-cathode was composed appeared to have a marked influence in determining the nature of the emitted radiation, and he even ventured upon the theory that the Röntgen rays might originate from the atoms of the anti-cathode themselves, and that the negative acceleration of the electrons of the cathode stream, instead of being the primary cause, might be merely instrumental in causing an emission of radiation, the exact nature of which was determined by the physical characteristics of the atoms receiving bombardment.

NOTICES OF BOOKS.

The General Character of the Proteins. By S. B. SCHRYVER, Ph.D., D.Sc. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1909.

THE properties of proteins, considered more especially from the point of view of their adaptability for methods of separating and isolating the substances, are briefly reviewed in this monograph. The physical properties—solubility in salt solutions, crystallisation, &c.—are first considered, and the general chemical characters in the second part. These, which are undoubtedly the most reliable for the separation and identification of different individuals, even in their present imperfectly worked-out state, are studied in detail, and many suggestions for what would probably be fruitful and is certainly much-needed research work could be gathered from this part of the book. The last section passes shortly over biological methods of differentiation, which cannot be regarded as generally applicable owing to their uncertainty and the time necessary for their completion; hence the author restricts himself to a brief summary of them, with references for further reading in the excellent bibliography with which the book is provided.

Suction Gas Plants. By C. ALFRED SMITH, B.Sc. (Eng.). London: Charles Griffin and Company, Ltd. 1909.

THE engineers who attended this course of lectures at the East London College were fortunate in hearing such an excellently clear and broad-minded view of the subject of suction gas plants, and many others who were unable to avail themselves of the opportunity will be glad to have in print, not only the lectures themselves, but also a summary of the inquiries made upon them, the lecturers' replies, and the correspondence which followed on them. The gas producer part of the suction gas plant is treated fully, and the details of the construction are made particularly clear. Methods of ensuring the maximum efficiency are discussed, and the advantages and disadvantages of the suction plant are also weighed. The question of the harmfulness of the effluent from a gas plant is also considered, and the possibility of injury to human or animal life is finally rejected. The diagrams with which the book is plentifully supplied are exceedingly well reproduced, and will undoubtedly help the reader very considerably; no graphic device which might make the subject clearer to practical men has been overlooked, and one great advantage of the illustrations is that they are easy to understand without continual reference to explanations or keys.

A Compendium of Food Microscopy. By EDWY GODWIN CLAYTON. London: Baillière, Tindall, and Cox. 1909.

THIS book is based upon the works of Dr. A. H. Hassall on Food Analysis, and consists of a revision of the microscopical portions of his writings. The original descriptions given by Dr. Hassall, who was a pioneer in recognising the value of the microscope as an instrument for the detection of adulterants in foods, &c., are often reproduced word for word, while the author has in some cases extended them and made some considerable additions. Articles of food such as prepared cereals, and nut-foods which have come into use in recent years, are treated in sections which are entirely new, and modern authorities have been freely consulted in order to make the book as complete as possible. The plates are reproductions of drawings, not microphotographs, which the author describes as indistinct and often useless; the drawings are certainly exceedingly clear and indeed diagrammatic in some cases. The reproductions of the slides of substances containing typical adulterants will be found very useful, and the adulterations have been carefully chosen with a view to including all those which are most probable. The arrangement of the plates opposite the descriptions is an excellent point in the book and will materially add to convenience in using it.

Das Ammoniak und Seine Verbindungen. ("Ammonia and its Compounds"). By Dr. J. GROSSMANN. Halle-a-S.: Wilhelm Knapp. 1908.

A VERY clear and systematic treatment of technical methods of preparing ammonia and its compounds is given in this monograph. All unnecessary details and padding are avoided, and antiquated methods are given no place in the text, with the result that room is found for an outline of methods of preparing and analysing all the important compounds besides gaseous and liquid ammonia. The preparation of ammonia from different sources, including its synthesis, is described in the first section, and a fairly full and detailed account of the testing of raw ammoniacal liquors is included. The division of each branch into theoretical, practical, and analytical parts makes it very easy to refer to the book and to find any required detail of information.

Tabellen zur Berechnung von Kalianalysen. ("Tables for the Calculation of Potash Analyses"). By Dr. R. EHRHARDT. Halle-a-S.: Wilhelm Knapp. 1908.

THE tables contained in this book include all those which are likely to be required in potash analysis, and are arranged in the most convenient form for rapid reference in the laboratory. Tables which are used in the potassium nitrate industry are also given, and the use of the book should greatly simplify and shorten the work of the alkali chemist, at any rate as far as calculation is concerned.

On the Calculation of Thermo-Chemical Constants. By H. STANLEY REDGROVE, B.Sc. (Lond.), F.C.S. London: Edward Arnold. 1909.

THIS book is an amplification of a number of short articles written by the author which have recently appeared in the CHEMICAL NEWS. Some of the papers have been considerably enlarged, and all have been subjected to a careful revision before being issued in book form. The author gives an outline of a method of calculating thermo-chemical constants which is more accurate than the usual methods, in which the value of certain links, for instance, the single ethane link is absolutely ignored. He assumes that each different link has a definite specific value, and working on this supposition has determined the molecular heats of combustion and formation of certain definite classes of organic compounds, using the formulæ obtained from general considerations. The data for the calculations are always taken from Julius Thomsen's experimental results. Incidentally he discusses Baeyer's Strain Theory,

of which he has found an important confirmation by studying the thermal behaviour of polymethylenes. A short criticism of Thomsen's method of calculating thermo-chemical constants concludes the book, which will be read with interest by physical chemists.

Organische Farbstoffe. ("Organic Dyes"). By Dr. H. WICHELHAUS. Dresden: Theodor Steinkopff. 1909.

IN the author's excellent work on chemical technology, "Vorlesungen über Chemische Technologie," it was impossible to do more than give an outline of some branches of chemical industry, and feeling that it would add to the usefulness of the book if the outline were somewhat filled in, Dr. Wichelhaus has prepared this supplement dealing with the organic dyes. In it he describes the properties and preparation on a commercial scale of various classes of organic derivatives which are of importance in the dyeing industry, and then passes to the dyes themselves, beginning with a short and clear account of what the term dye denotes. The properties of the individual dyes more particularly from a chemical point of view are discussed, as well as their preparation, and a short *résumé* of methods of using them, calico printing, &c., is included. The book, though short, gives a complete summary of methods of obtaining synthetical dyes and of applying both natural and artificial colouring agents, and is a useful handbook for the chemist in dye-works.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlviii., No. 14, April 5, 1909.

New General Method of Preparing Alcoholic Amines.—Paul Sabatier and A. Mailhe.—When ethyl alcohol acts on ammonia in presence of thorium or blue tungsten oxide, ethylamine is produced. The primary amine also reacts in presence of the catalysing oxide, giving a secondary amine from which the tertiary amine may also result similarly. This new method of synthesising amines can be applied to aromatic alcohols and to secondary alcohols.

Formation of Graphitic Oxide.—Georges Charpy.—Graphite and amorphous carbon have been distinguished by their reaction with Brodie's mixture (fuming nitric acid and potassium chlorate). Amorphous carbon is dissolved and graphite gives a yellowish insoluble substance, graphitic oxide. The author has studied the action of different oxidising mixtures on natural and artificial specimens of carbon, and has found that graphitic oxide may be isolated from amorphous carbons. Hence the identification of graphite cannot be based upon oxidation reactions, and certain carbons, notably the product of the decomposition of graphitic oxide by heat (pyrographitic oxide), and the carbon extracted from steel by dissolving the metal in metallic salts, must be classed in the category of graphites.

Preparation of Pure Iodic Anhydride.—Marcel Guichard.—The preparation of iodic acid by the oxidation of iodine with potassium chlorate or fuming nitric acid does not give yields which are satisfactory either as regards quantity or purity. On the other hand, dry, or better still moist, iodine is very easily transformed into iodic anhydride with a rise of temperature by the action of fumes of nitric anhydride. The yield is ten times greater than with the direct action of the fuming acid, and amounts to 40 per cent of the theoretical yield. The product can also be obtained in a very pure state, for the oxidising agent is distilled during the experiment, and it would also be quite easy to make the iodine sublime in the tube in which the oxidation is effected.

Total Synthesis of Laudanosine.—Amé Pictet and M. Finkelstein.—Laudanosine can be synthesised by the following operations:—(1) Preparation of homoveratrylamine, $(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3-\text{CH}_2-\text{CH}_2-\text{NH}_2$, by the action of sodium hypobromite on dimethylhydrocaffeic amide, $(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3-\text{CH}_2-\text{CH}_2-\text{CO}-\text{NH}_2$; (2) preparation of homoveratrylic acid from eugenol and transformation into the chloride $(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3-\text{CH}_2-\text{COCl}$; (3) combination of this chloride with homoveratrylamine in presence of caustic soda, thus obtaining homoveratryl-homoveratrylamine, $(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CO}-\text{CH}_2-\text{C}_6\text{H}_3(\text{OCH}_3)_2$; (4) treatment of this compound with phosphoric anhydride when dihydropapaverine is formed; (5) transformation of dihydropapaverine into its chlormethylate and reduction of the latter by tin and hydrochloric acid. The product is racemic methyltetrahydropapaverine, which under the action of quinic acid gives the dextroisomer, which is identical with natural laudanosine.

Catalytic Preparation of Ketones.—J. B. Senderens.—Anhydrous ThO_2 is a catalytic agent which very readily converts free acids into acetones. Thus diethylketone, $\text{C}_2\text{H}_5-\text{CO}-\text{C}_2\text{H}_5$, is rapidly obtained from propionic acid. In the case of formic acid formic aldehyde is obtained according to the equation

$$\begin{array}{c} \text{HCO}\cdot\text{OH} \\ \text{HCO}\cdot\text{OH} = \text{H}_2\text{O} + \text{CO}_2 + \text{HCHO} \end{array}$$

But formic acid is decomposed at 260° into carbon monoxide and water, and with alumina these are the only products. With thoria, however, the liquid obtained is a mixture of formaldehyde and unchanged acid.

Formation of Peroxides in the Oxidation of Organo-Magnesium Compounds.—H. Wuyts.—The author has shown that when ethereal magnesium solutions are exposed to the action of oxygen, peroxide compounds are formed. Thus a mixture of magnesium ethyl bromide and toluene when treated with dry oxygen at a low temperature becomes capable of setting iodine free from an acetic solution of potassium iodide. Hydroquinone gives an intense coloration with a magnesium organo-compound in pure oxygen, while in hydrogen no coloration is produced. In absence of air diphenylamine gives a colourless liquid, while in air a blue coloration is produced, and a blue coloration is also obtained by ethyl sulphide and paradimethylaminophenyl. These colour reactions can most easily be explained by assuming the presence of peroxidised compounds.

Tetrahydronaphthylglycols (*cis* and *trans*) and their Combination.—Henri Leroux.—Dibromide of dihydronaphthalene and silver acetate in boiling acetic solution yield an ethereal solution from which two substances of formula $\text{C}_{10}\text{H}_{12}\text{O}_2$ can be isolated. The one which fuses at 118° is the *trans*-isomer, and the other fusing at 140° the *cis*-isomer. The proportion of *cis* and *trans* isomer formed varies according to the circumstances of the experiment, and apparently the dibromide of dihydronaphthalene itself is a combination of *cis* and *trans* isomer.

MISCELLANEOUS.

Association of Teachers in Technical Institutions.—The Annual Conference of the Association will be held this year at Liverpool. The conference will be opened on Whit-Monday by Alderman Wm. Oulton, Chairman of the Liverpool Education Committee. On Tuesday, June 1st, the proceedings will be opened by the Right Hon. the Lord Mayor of Liverpool, H. Chaloner Dowdall, Esq. On Tuesday afternoon there will be a reception by the Lord Mayor and Lady Mayoress at the Town Hall. On Monday morning the Presidential Address will be delivered by J. Wilson, M.Sc., and during the conference important resolutions relating to the improvement of technical education will be discussed.

Presentation to Prof. Senier.—The old Galway students of Prof. Senier have just presented him with an Address, encased in a silver casket, expressing their pleasure at the recent action of the Royal University in conferring upon him the honorary degree of Doctor of Science in recognition of his services to Science and to University Education in Ireland.

Royal Institution.—On Tuesday next, June 1, at 3 o'clock, Dr. F. Gowland Hopkins begins a course of two lectures at the Royal Institution on "Biological Chemistry"; on June 3, Prof. W. E. Dalby commences a course of two lectures on "A Modern Railway Problem—Steam v. Electricity"; and on Saturday, June 5, Dr. F. F. Blackman delivers the first of two lectures on "The Vitality of Seeds and Plants"—(1) "A Vindication of the Vitality of Plants"; (2) "The Life and Death of Seeds." The Friday Evening Discourse on June 4 will be delivered by Prof. J. A. Fleming on "Researches in Radioteleggraphy"; and on June 11, by Prof. Sir James Dewar, on "Problems of Helium and Radium." An extra discourse will be delivered on June 18 by Mr. A. Henry Savage Landor on "A Recent Visit to the Panama Canal."

A New Company has been formed entitled the Cowper-Coles Engineering Co., Ltd., with a working capital of £40,000, and its offices are at Grosvenor Mansions, 82, Victoria Street, S.W. The company has been registered as a private company, and no issue will be made to the public. The objects of the company are to develop the business of Sherard Cowper-Coles and Co., Ltd., and to carry on the work of electro-metallurgists and chemical engineers. The company will have a large exhibit of their special products, machinery, and apparatus at the forthcoming London International Exhibition. Amongst other things will be exhibited in operation a process for welding aluminium, a regenerative process of electro-galvanising, a centrifugal process for the direct production of copper sheets and tubes, a process of vapour-galvanising; samples and specimens of Mr. Sherard Cowper-Coles' process for producing iron sheets and tubes without smelting or rolling will also be exhibited, and parabolic reflectors for locomotive and motor car headlights and searchlights, the latter constructed so as to throw yellow and white beams of light, which have great advantages for naval and military purposes. Samples and specimens of the firm's process for ornamenting and decorating metallic surfaces, and a variety of other electro-chemical processes and apparatus will also be shown.

MEETINGS FOR THE WEEK.

TUESDAY, June 1st.—Royal Institution, 3. "Biological Chemistry," by F. Gowland Hopkins, F.R.S., &c.

THURSDAY, 3rd.—Royal Institution, 3. "A Modern Railway Problem—Steam v. Electricity," by Prof. W. E. Dalby.

Chemical, 8.30. "Wolcott Gibbs Memorial Lecture," by F. W. Clarke. "Molecular Weight of Tetraethylammonium Bromide and the Atomic Weight of Carbon," by A. Scott. "Rate of Formation of Azo-derivatives from Benzenoid Diamines," by V. H. Veley. "Synthesis of Substances allied to Cotarnine," by A. H. Salway. "Monomethylfructose and its Derivatives—Constitution of Fructosediacetone," by J. C. Irvine and A. Hind. "Optically Active 8-Oximinohexahydrobenzoic Acid and the Configuration of the Oximino-group," by W. H. Mills and Miss A. M. Bain.

FRIDAY, 4th.—Royal Institution, 9. "Researches in Radio-telegraphy," by Prof. J. A. Fleming, F.R.S.

SATURDAY, 3rd.—Royal Institution, 3. "The Vitality of Seeds and Plants," by F. F. Blackman, F.R.S., &c.

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SEVENTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

THE Seventh International Congress of Applied Chemistry was opened on Thursday, May 27th, at the Albert Hall. The Prince of Wales, Patron of the Congress, presided, and he was accompanied by the Princess of Wales. The arena of the hall was filled to overflowing with a company of more than 2000 eminent chemists and no less eminent manufacturers from all parts of the civilised world. Their Royal Highnesses were escorted on to the platform by Sir Henry Roscoe, Hon. President, and Sir William Ramsay, Acting President, of the Congress, while the organ played "God Bless the Prince of Wales." The Prince took the Chair and opened the proceedings. On his left were the Princess of Wales, Dr. Harvey W. Wiley, chief representative of the United States, M. Armand Gautier, member of the Institute, representing France, and Professor E. Paterno, representing Italy. On his right were Sir Henry Roscoe, Sir William Ramsay, Professor Dr. O. N. Witt, representing Germany, and Professor Arrhenius, representing Sweden. Among those present on the platform were the American Ambassador, the French Ambassador, the Chinese and Japanese Ambassadors, the Portuguese and Danish Ministers, the Duke of Northumberland, Viscount Wolverhampton, Lord Rayleigh, Lord Strathcona, Mr. Walter Runciman, M.P., the Master of Elibank, M.P., Sir William Crookes, Sir James Crichton-Browne, Sir James Dewar, Dr. Ludwig Mond, and Professor Frankland.

HIS ROYAL HIGHNESS, having taken the Chair, was warmly cheered on rising to declare the Congress open. He said:—

Your Excellencies, my Lords, Ladies, and Gentlemen—It gives me much pleasure, as Vice-Patron, to preside over the first meeting of this important International Congress of Applied Chemistry, and the Princess of Wales is very glad to accompany me on this occasion.

Delegates and members, including many ladies, have come, not only from every country in Europe, but from all parts of the world, literally from China to Peru. Six congresses have already been held in the various capitals of Europe. This is the first time that you have assembled in London, and in the name of the King, who is Patron of the Congress, I offer you his Majesty's most hearty welcome. His Majesty is very glad to think that the foreign representatives will visit Windsor Castle during their stay in this country.

The main object which you all have in view is, I assume, to discuss in your numerous sections the many topics of interest and importance that are continually arising, owing to the marvellous discoveries which the science of chemistry, both pure and applied, is making from day to day.

Those interested in some special branch meet in the different sections their *confrères* from other lands, to their mutual benefit. In the larger gatherings, which I am glad to see have been arranged by the Committee, members will have further opportunity of social meeting. These conferences, whether of a scientific or of a more intimate character, between men living in distant lands, all working for the same object, although under different conditions, cannot but be favourable to the progress of science and to the industries to which many of you have devoted your lives, as well as to the general peace of the world.

I fully appreciate the important part which chemistry plays in almost every branch of modern industry. We all recognise that without a scientific foundation no permanent superstructure can be raised. Does not experience warn us that the Rule of Thumb is dead, and the Rule of Science

has taken its place; that to-day we cannot be satisfied with the crude methods which were sufficient for our forefathers, and that those great industries which do not keep abreast of the advance of science must surely and rapidly decline?

On behalf of the Princess and for myself I offer our cordial greeting to the members of the Congress, and I earnestly trust that great results may accrue from your deliberations. I now have much pleasure in declaring the Seventh International Congress of Applied Chemistry open. (Cheers).

SIR HENRY ROSCOE, the Honorary President, was then called upon by his Royal Highness. He said he rose in the first place to express on the part of British chemists a hearty English welcome to their *confrères* who had assembled from all parts of the world. He rose also to ask the members and delegates to express their thanks to the Prince and Princess of Wales. A formal vote of thanks was unnecessary, for the thanks came from all their hearts for the grand send-off which their Royal Highnesses had given the Congress, and for the kind and felicitous terms in which the Prince had opened the proceedings. (Cheers).

SIR WILLIAM RAMSAY said—Following the lead of the Prince of Wales, it falls to my lot to bid our guests welcome to this Congress of Applied Chemistry, the seventh which has taken place since the first meeting in Brussels, in 1894. Our last meeting was held in Rome, where his Majesty the King of Italy was graciously pleased to occupy the position which his Royal Highness has kindly filled to-day. There the Honorary President was the world-renowned Cannizzaro, the publication of whose views, almost exactly fifty years ago, effected a revolution in chemical thought, and made clear what was formerly obscure and involved. It is delightful to think that Professor Cannizzaro, though unable to take part personally in this Congress, is strong and well, and in full possession of all his faculties. May he long be spared to adorn the science he has so greatly enriched by his discoveries and by his teaching! Professor Paterno was then Acting President, and I take this opportunity of bidding him welcome to England. I should also like to welcome the small band of young Italians, to whom the surplus of the funds collected for the Sixth Congress has given an opportunity of visiting England. Professor Witt, the Acting President of the Fifth Congress, which was held at Berlin, is also our guest here. We thank him for coming, and for the great help he has given the Organising Committee by his advice, and we trust that he will find his sojourn in this country, to which he has connected himself by marriage, a pleasant one. Since our last meeting, the Honorary President of the Fifth Congress, M. Berthelot, and the Acting President, M. Moissan, have been taken from us. Having had the privilege of the friendship of these two great men, I cannot help expressing a feeling of great personal sorrow, which I know will be echoed by many present, that we have lost them. Berthelot was full of years and honours; Moissan we had hoped to keep among us for long in health and strength. France has indeed been sadly bereaved during the past few years; but we are glad to welcome here M. Lindet, the President of the first French Congress. It is impossible to draw a hard and fast line between scientific and technical chemistry. Chemistry is, above all, a practical science, although in recent years it has tended to become more and more a branch of applied mathematics. And the principles remain the same, and, indeed, the methods are only slightly varied, whether the apparatus used are beakers, test-tubes, funnels, and flasks, or tanks, filter-presses, and autoclaves. The chief difference between the pure science and its application consists in a satisfactory answer to the question, all important to the technical chemist, but wholly irrelevant to the man of science—will it pay?

On the answer to that question the commercial success of a process depends, but in its essence chemistry, whether scientific or industrial, is one. This, I think, has hardly been realised in a practical manner on this side of the

channel, or, indeed, on the other side of the Atlantic. But our Continental friends have long seen and acted on the conviction that the industrial prosperity of a country can best be advanced by a close friendship and constant association between the technical and the practical workers, between the university and the factory, between the pure and the applied science. Congresses like the present can teach us much; if we learn this lesson from them, we shall have gained a valuable national asset.

M. Berthelot, in an Address given on an occasion similar to this, pointed out how far the comfort, prosperity, and advancement of the human race depends on our science. Originally confined to alchemists and to so-called philosophers, there are now few regions which are not illuminated by the light of chemistry. Its ultimate goal is to render an intelligible account of the nature of the universe in which we are placed, and the composition of the stars has been revealed by its efforts. Still, while striving to reach that somewhat transcendental goal, we are able to pluck many flowers by the way—flowers which not only please us by their beauty and fragrance, but which, in many cases, are of practical use in alleviating our suffering and administering to our comfort in every aspect of our lives.

It has often been said that science is cosmopolitan, and knows no country. The existence of such a Congress as this is in itself a proof of the truth of this saying. We are favoured by the presence of representatives from every civilised State in the world. We are met together to discuss how best to develop the special branches of chemistry to which we devote our lives; how to further their progress, and to mark the level to which they have already attained. A glance at our programme will reveal the many-sidedness of our endeavours. There is a city on the other side of the Atlantic whose motto, I think, is one of the noblest imaginable. It has the sanction of Scripture, and it is eminently practical. "Philadelphia Maneto!" Let brotherly love continue. (Cheers).

Sir WILLIAM RAMSAY then addressed words of friendly greeting to the foreign delegates in French, German, and Italian.

Dr. HARVEY W. WILEY (chief Government Chemist of the United States) was then called upon by his Royal Highness to speak for America. He said:—The assembling of the Congress is illustrative of the progress of the age. Chemistry is the fundamental science, in that it treats of the ultimate nature of things. It is also the science of most productivity, because it is applied in all the industries. In so far as I know there is not a single industry of any importance to man that does not claim tribute of chemistry. The art of agriculture, most of all, lies at the very foundation of human happiness and existence. There is no more apt illustration of the utility of chemistry than to say that were its principles unknown and unapplied the teeming millions of the globe would at this moment be unclad and starving. But we are too much concerned at all times with mere material progress and prosperity. That nation is deemed most prosperous which is most wealthy, and the view-point of applied chemistry is too often restricted to the immeasurable value which chemistry has been to the increase of wealth.

But there is a more important service of chemistry to man even than that. In later years this science has been utilised not only to improve the engines of war, but far more to develop new services for man. The great strides now making to apply the principles of prophylaxis in medical science are largely due to the services of chemistry. In fact, sanitation is principally a chemical problem; pure food, pure air, pure water, insuring pure activity of mind and body, and curing disease by evading it, and prolonging by many years the most valuable part of human life, viz., its period of maximum endeavour. And to this great work chemistry is giving its most precious contributions. In another important particular chemistry is rendering service to humanity. It has undertaken to improve the morality of man. All science has a stimulating effect on morality, because science seeks only the truth; but chemistry has

already made great progress in improving the morality of trade. It detects frauds and adulterations in all articles bought and sold. It exposes the manufacturer and the dealer who makes and sells any article deleterious to man, or under a false name or representation, to public scorn and to the penalties of the law.

There are no means of bringing nations to a better understanding of their mutual hopes and endeavours, no better ways of preserving international peace and amity, than by securing the fruits of science in its application to all industries. In this hall are assembled delegates from all countries of the world. We have come to compare notes of progress, to be mutually helpful in the work for the benefit of man which we are trying to do. Our purpose is to ease, if possible, the suffering of the poor, to lighten to some extent the task of labour by making it more fruitful, to prevent sickness and promote health, to prevent crime and punish wrong-doing, to eliminate from commerce every species of fraud and misrepresentation, and in this great work we are inspired by the patronage of your Royal Highnesses. (Cheers).

Professor ARMAND GAUTIER, Professor at the Sorbonne, Member of the Académie des Sciences, speaking in French, said the Minister of Public Instruction and the French chemists had asked him to express the sympathy which they had for the science and genius of this great country. If revolutions and politics in the past had been able to separate the two countries, the appreciation of noble qualities and the tradition of a long common culture had contributed little by little to unite them more even than treaties. Although generations had passed, it was not forgotten that it was to Priestley that the world owed the discovery of oxygen; to Cavendish, that of hydrogen; to Dalton, the law of multiple proportions and the fundamental notion of atoms; to Humphry Davy, acquaintance with the alkali metals and the miner's safety lamp. In the development of science and industry England and France had remained the initiating nations—always worthy rivals, but never enemies. After Nicolas Leblanc invented in France the manufacture of artificial soda from sea salt, the industry was made perfect in this country owing to the researches of Hurter, Hargreaves, and Gossage. Later, Deacon and Weldon greatly perfected the manufacture of chlorine and of chlorine bleaching agents. Fox Talbot discovered photography on paper and popularised photography invented by Niece and Daguerre. In our day, following the researches of the great British scientist Faraday, Cailletet in France succeeded in liquefying the permanent gases. While at Lyons Verguin was finding out fuchsin by chance, they were learning that he was in this field preceded by Perkin, who a little before had obtained mauveine, the first colouring matter derived from coal-tar, thus opening the fruitful career in which so many others were to follow. In this country he could not forget the names of Lowthian Bell, William Siemens, Sir Henry Bessemer, Thomas Gilchrist, and the celebrated inventor of explosives, Sir Frederick Abel. To that list he would add the name of one who so greatly perfected the manufacture of pottery and ceramic ware, Josiah Wedgwood. Despite all events and sometimes political errors, England and France had always walked side by side in the way of science and industry. The countrymen of the Lavoisiers, the Pasteurs and the Berthelots were happy to come to-day and offer a just tribute of homage to the countrymen of the Cavendishes, the Davys, and the Faradays, bringing to British science and activity the expression of its admiration and sympathy. (Cheers).

The PRINCE next called on Professor Dr. O. N. WITT, who, speaking in German, said that in the name of the Imperial German Government and the Prussian Royal Government, and also on behalf of the German Chemical Society, whose President he had the honour to be, he expressed the hope that the Congress would not only, by the work carried out, be as important as its predecessors, but would signify further progress in that branch of science

in which it was interested. This Congress was the promoter of friendly understanding and of noble emulation between all nations, and it was to be congratulated on enjoying the patronage of those who direct the destinies of their people. Thus to-day, when the Congress opened in a land which was the first to boast of having developed a complete chemical industry, its noble ruler had honoured it with his favour. In his capacity as President of a former Congress he thanked His Royal Highness on behalf of all who had laboured for the Congress, and asked him to convey those thanks to His Majesty. He could only express the hope that the results of their deliberations would be in every way fruitful. (Cheers).

Professor E. PATERNO, speaking in Italian, said that as President of the sixth Congress, at which, held in the eternal city of Rome, London had been chosen as the seat of the present Congress, it was his duty to pronounce an inaugural greeting to that imposing gathering of illustrious scientists and practical and expert manufacturers. In the name of the Government of His Majesty the King of Italy, of the Royal Academy of the *Lincei*, and of the Italian Chemical Society, he offered the warmest wishes for the success of the Congress, and returned hearty thanks to the organising committee in London for their hospitable and genial reception. They were all bound to respond enthusiastically to an invitation from the country which gave to chemistry Boyle, Black, Cavendish, Priestley, Wollaston, Dalton, Davy, Faraday, and Graham. Even in the busy, noisy, bewildering rush of London life men of science yet knew how to find the tranquillity and quiet necessary for the investigation and discussion of the most abstruse problems of philosophy and science. He concluded by saying that Italians cherished another sentiment not less warm in the memory of the hospitality and succour found in this classical land of liberty by the fathers of their political regeneration.

Professor S. A. ARRHENIUS, of the Stockholm University, spoke for all the remaining countries. Addressing his listeners in English, he said that this country was the classical land of applied chemistry. It was in England that Priestley, for the first time, studied the most important of all chemical processes, and it was in this country, and especially in London, that great and successful efforts were made to improve hygiene, as the result of which London had the lowest death-rate among the large cities of the world. He was inspired with the confident hope that this Congress would have the most beneficial results for culture and humanity.

Government Delegates.

The countries represented and the official Government delegates to the Congress are as follows:—

Algeria—M. Pouget.
Argentina—Dr. Francisco P. Lavalle.
Austria—Hofrat Dr. F. W. Dafert, Regierungsrat Friedrich Strohmer.
Belgium—Prof. van Engelen, Prof. J. Jacobsen, Prof. Jorissen, Prof. Krutwig, Prof. van Laer, M. François Sachs, M. S. Starsart, M. V. Watteyne, M. Maurice Duyk.
China—Mr. On Kouanze, Mr. Yu Tung Kwai.
Colombia—Signor Don Francisco Becerra.
Chile—Señor Don Alejandro Bertrand, M. Lemetayer, Dr. Edwyn P. Reed, Dr. Luis E. Mourgues.
Denmark—Prof. E. Büllman, M. G. A. Hagemann, M. N. L. Hansen, Captain M. G. Hoffmann, M. C. Jacobsen, Prof. N. Steenberg.
Ecuador—Señor Don C. Nevares.
France—M. le Chatelier (Member of the Institute), M. Armand Gautier (Member of the Institute), M. Gayon (Bordeaux), M. Haller (Member of the Institute), M. Hougounenq (Lyons), Prof. Urbain (Paris), Prof. Vignon (Lyons), Captain Nicolardot, M. Bonjean, Dr. Bordas, M. Dienert, M. Eugène Roux, M. Chesneau, M. Etienne, M. René Feret, M. Vieille, M. Bruno, M. Dupont, Dr. Ricard, M. Silz, M. Halphen, M. Lodin.

Germany—Prof. Dr. O. N. Witt, Dr. von Bottinger Dr. Mente, Dr. Haupt-Buntzen (Saxony).

Greece—M. Kambas, Dr. L. Oekonomides, Dr. P. D. Zacharias.

Hungary—M. Nikolaus Gerster, Dr. Fritz von Konek-Norwall.

India—Mr. David Hooper.

Italy—Prof. Villavecchia, Comm. Giacomo Ciamician (Bologna), Comm. Arnaldo Piutti (Naples), Signor Luigi Belloc, Prof. Massimo Tortelli (Genoa), Prof. E. Paterno.

Japan—Prof. Mitsuru Kuhara, Prof. Nishikawa.

Netherlands—Prof. H. T. Hamburger (Gröningen), Prof. A. F. Hollmann (Amsterdam), Dr. Hoogewerff (Delft).

Norway—Prof. O. H. B. Birkeland, M. Samuel Eyde, Prof. J. R. F. Sebelien.

Portugal—Dr. Hugo Mastbaum.

Rumania—Dr. L. Edelceanu.

Russia—Prof. Prianschnikov.

Servia—Prof. Marco T. Lecco.

Spain—Prof. E. Pinerua y Alvarez, Don José Rodriguez Mourelo, Prof. A. y Peralta.

Sweden—Prof. P. Klason.

Switzerland—Dr. G. Bosshard (Zürich), M. F. Reverdin (Geneva), Dr. F. Schaffer (Berne).

United States—Dr. Harvey W. Wiley, Dr. L. H. Baekeland (New York), Dr. Charles Baskerville (New York), Dr. Frank W. Clarke, Dr. Allerton S. Cushman, Dr. W. L. Dudley (Tennessee), Dr. Morris Loeb (New York), Dr. William H. Nichols (New York), Dr. Albert Plant (New York), Dr. Maximilian Toch (New York), Mr. David P. Day.

Reception at the Guildhall.

On Wednesday evening, May 26th, the Lord Mayor entertained some of the delegates at dinner at the Mansion House. There were also present:—Lord Alverstone, Sir John Brunner, M.P., Sir William Ramsay, Sir William Crookes, Sir William Huggins, Sir Archibald Geikie, Sir Henry Roscoe, Sir James Dewar, Sir Andrew Noble, Sir James Crichton-Browne, Sir Boverton Redwood, Dr. E. K. Muspratt, Dr. T. E. Thorpe, Prof. Dixon, M. Armand Gautier, Geheimrath Prof. Dr. O. N. Witt, Dr. W. H. Wiley, Prof. Meldola, Prof. R. Nasini, Prof. Tawildaron, Prof. Lecco, Dr. Bokors, Prof. Dr. Lindet, Prof. Dr. Duisberg, Dr. E. P. Reed, Prof. Piutti, Prof. Haller, Dr. Zacharias, Dr. Halleman, and Mr. W. Macnab, the Hon. General Secretary of the Congress. The Lady Mayoress and the Misses Truscott were also present.

Afterwards in the Guildhall the Lord and Lady Mayoress gave an official reception to the Congress, the music being supplied by the band of the Royal Artillery. In the new Council Chamber a concert was given under the direction of Mr. Arthur Weston, while Lawler's Ladies' Orchestra provided instrumental music in the Library. Dancing took place in the Art Gallery. During the evening the company was augmented by the presence of a number of the German municipal visitors.

The guests, who numbered about 2000, were received by the Lord Mayor, the Lady Mayoress, and the Sheriffs. The whole of the arrangements were made and carried out under the direction of Mr. W. H. Pitman, the Chairman, and the Members of the City Lands Committee.

After the reception was over the guests dispersed to various parts of the Guildhall, where entertainment of different kinds had been provided. The City Corporation, mindful of the reverence due to its antiquity, gave an exhibition of various items bearing on its honoured and ancient history.

The City Treasures on View.

The German delegates in particular took delight in a deed bearing the signature of Shakespeare, and the jewelled sceptre, the seal of office of the Mayoralty, the purse, and a collection of civic medals and livery company badges also came in for close inspection, especially by the feminine

portion of the audience. Many ancient charters were on view, including that in which King John granted the Shrievalty of London and Middlesex to the citizens of London in 1199, and that in which the same king, who seems to have done one good thing in his time, gave them, in 1214, the right to elect their mayor. Many ancient books were on exhibition, such as the Liber Albus, compiled in 1419 by John Carpenter, the worthy Town Clerk whose name now appears, alas! on the Embankment tram tickets, and the Husting Roll of 1252-4.

On Thursday, May 27th, Mr. Lewis Harcourt, M.P., on behalf of the Government, held at the Foreign Office a reception of the delegates to the International Congress of Applied Chemistry. The reception rooms and staircase were elaborately decorated with flowers and tall palms. Over a thousand guests attended, including most of the members of the Ministry and Opposition, and a number of ex-Ministers. The Court was largely represented, as also were the services, whilst a number of Foreign Ambassadors and Ministers attended.

SECTIONAL PROCEEDINGS.

The Business work of the Congress commenced on Thursday, May 27th, when the following papers were read:—

SECTION II.—Inorganic Chemistry and Allied Industries.

The President (Dr. LUDWIG MOND, F.R.S.) delivered his Address on "The Metallic Carbonyls."

SECTION IVa. 2.—Physiological Chemistry and Pharmacology.

The President for the day (Prof. CUSHNY), after welcoming the members of the section, referred to the great loss which the section had sustained by the death of Dr. Gamgee. Dr. Gamgee had taken such great interest in the organisation of the section, and by his energy and perseverance had formed it into a special sub-section of organic chemistry. His great desire was to see Physiological Chemistry and Pharmacology firmly established as a separate and independent section in future Congresses.

It was resolved by the members of the section that the Secretary should communicate with Mrs. Gamgee and express to her their deepest sympathy in her loss.

SECTION V.—Industry and Chemistry of Sugar.

The President (Sir RICHARD C. GARTON) welcomed the members of the Section and gave a few introductory remarks on the programme which had been prepared.

SECTION III.a.—Metallurgy and Mining.

After the delivery of the Presidential Address by Sir HUGH BELL, the following papers were communicated:—

M. A. Portevin (France)—"Influence des traitements thermiques sur les alliages de cuivre."

L. Guillet (Paris)—"Traitement thermique des produits metallurgiques autres que les produits siderurgiques." The following gentlemen contributed to the discussion on these papers:—Dr. Desch, Dr. W. Rosenhain, Prof. H. Louis.

Dr. T. K. Rose (London)—"Electrolytic Refining of Gold." Alfred James (London)—"The Cyanide Process." The following gentlemen contributed to the discussion on this paper:—H. Louis and H. M. Ridge.

C. O. Bannister, A.R.C.M. (London)—"Modern Methods and Improvements in the Extraction of Zinc from Ores."

H. O. Hofman (U.S.A.)—"Some Developments in Blast Roasting." The following gentlemen contributed to the discussion on this paper:—Messrs. A. Rayman, H. M. Ridge, Prof. Schiffrer.

On Friday, May 28th, the following papers were read:—

SECTION II.—Inorganic Chemistry and Allied Industries.

H. Le Chatelier—"Etudes sur la decomposition des ciments."

P. Lebeau—"Gaz toxiques degages par le ferrosilicium."

R. Feret—"L'essai Chimique des Pouzzolanes."

E. P. Alvarez—"Reactions du zinc, du nickel, et du cobalt utilisables en analyse."

D. Crispo—"Sur une nouvelle reaction donnant lieu a la production de Carbonate de Soude."

GINNO GALLO—"Microscopic Study of Mortars."

Sir James Dewar—"Rate of Production of Helium from Radium."

SECTION III.b.—Explosives.

After the delivery of the Presidential Address by Sir ANDREW NOBLE, Bart., K.C.B., the following papers were communicated:—

Capt. Desborough—"Administration of the Explosives Act." Discussed by C. O. Lundholm, Capt. Lloyd, and Prof. Cronquist.

Prof. W. Will—"Prufung von Sprengstoffen im Hinblick auf deren Zulassung zum Verkehr."

Prof. Leaze—"Prufung von Sprengstoffen im Hinblick auf deren Zulassung zum Verkehr." In the absence of the author, this paper was communicated by Dr. Kast. Discussed by Herr R. Sohlman.

Dr. Otto Poppenberg—"Ueber die Zersetzung von Sprengstoffen, ihre Verbrennungswarme und Explosions-temperatur."

Dr. H. Kast—"Prufung von Sprengstoffen mittelst des Fallhammers."

SECTION IV.a (1).—Organic Chemistry and Allied Industries.

A. M. Nastukoff—"Chemical Composition of the Lubricating Oils."

M. Z. Jovitchitch—"Die Kondensations produkte von Athylen und Acetylen mittels der dunklen Electricischen Entladung."

M. Barbet—"Rectification continue et purification des hydrocarbures."

G. Koller—"Chlorine Derivatives of Ethane and Ethylene and their Industrial importance as Non-inflammable, Non-combustible, and Non-explosive Solvents."

C. Baskerville—"Oil Shales of Canada."

A Discussion was opened by W. H. Coleman on "The Prospects of the Tar Industry, having in view the Probable Increase in the Production of Tar consequent on the Adoption of the By-product Coke Oven."

SECTION IV.a (2).—Physiological Chemistry and Pharmacology.

Hardy—"Source of the Electric Discharge on Colloidal Particles."

Bayliss—"General Properties of Colloids as exhibited by certain Dye-stuffs."

Freundlich—"Ueber die bedeutung der adsorption fur die physiologische chemie."

Bechhold—"Die Kolloide in der biologie u medezin."

Botazzi—"Proprieta di alcuni colloidi organici." Discussed by Messrs. A. Gautier and Bechhold.

Friedenthal—"Ueber titration und H x i onengehalts bestimmung mit indicatoren." "Unterschiede im Bau von Kernstoffen und Eiweiss." Discussed by Messrs. Drucker and Rothmund.

Marino—"Le Oscellazioni periodiche dell' attivita dell' emulsina sotto l'influenza della luce solare."

SECTION V.—Industry and Chemistry of Sugar.

G. C. Borgnino (Ravenna)—"Origini dell'Industria dello fuccherio in Italia." Discussed by Mr. F. Sachs.

H. P. Agee (New Orleans)—"The Cane Sugar Industry of Louisiana."

- A. H. Bryan (Washington)—"The Beet Sugar Industry of the United States."
W. D. Horne (Yonkers)—"History of Sugar Refining in the United States." Discussed by Messrs. Herzfeld, Horne, and Fischmann.
Theo. Brooks (Guatnamo)—"Review of the Conditions, Progress, and Future of the Sugar Industry in Cuba." Discussed by Messrs. H. Pellet, Stein, and Brooks.
Noel Deerr (Honolulu)—"The Cane Sugar Industry in the Hawaiian Islands." Discussed by Messrs. H. Pellet and Kobus.
F. Zerban (Lima)—"The Cane Sugar Industry of Peru." Discussed by Messrs. Saillard and Fischmann. On the motion of Prof. Herzfeld, a Committee was appointed, consisting of Messrs. Dupont, H. Pellet, Fischmann, Sachs, and Saillard, to take steps towards furthering the movement for obtaining a reduction of the taxes on sugar advocated by MM. Dupont and Fischmann.
F. Dupont (Paris)—"Moyens de developper la consommation du sucre." Discussed by Messrs. Saillard, Fischmann, Herzfeld, Sachs, and Dupont.
—Kandelik and T. Urban—"Ueber die Variabilität des Stickstoffgehaltes in den Zuckerrubenwurzeln."

SECTION VI.a.—Starch Industry.

- Dr. L. T. Thorne—"Determination of Starch by the Acid Method." Read by Julian L. Baker. Discussed by Messrs. Lindet and Millar.
Dr. G. Parow—"Die Herstellung der Trockenkartoffel und ihre Verwendung." Discussed by Dr. Van Laer, Mr. Baker, Mr. Whympier.
MM. Arpin, Ringelmann, et Lindet—"Resultats generaux fournis par le petrisage mecanique." Discussed by Messrs. Whympier and Watkin.
W. Jago—"Bleaching and Conditioning of Flour." Read by Julian L. Baker. Discussed by Messrs. Holderer, Baker, Watkin, and Humphries.
MM. Kayser et Radow—"The Yeast of the Baking Trade."

SECTION VI.b.—Fermentation.

President for the day, Colonel J. GRETTON, M.P.

- Mons. Guillaume—1. "Auto-chauffage de la Colonne rectificatrice, en distillation-rectification directe et continue, par le passage des flegmes bruts sortant en vapeurs de la colonne a distiller pour aller a l'epurateur a bas degre."
2. "Procédé de réglage automatique de la sortie de l'alcool assurant, à la fois, la fixité du degre audit alcool, et la permanence de l'épuisement des vinasses, ou des flegmasses dans les appareils de distillation-rectification directe et continue, de rectification continue, ou tous appareils produisant de l'alcool a haut degre."
3. "Nouveaux plateaux analyseurs pour colonnes a distiller et a rectifier."
Mons. Mariller—"Etude des condenseurs employes en distillation et rectification."
In the author's absence this paper was read by Prof. Levy—"Les nouveaux appareils de Distillerie essayes a l'Ecole de Douai." Discussed by Messrs. Guillaume and Holderer.
Mons. Reviere—(1) "Fabrication et emplois industriels des melasses depotassees; (2) Transformation des fluosilicates alcalins en carbonates." Discussed by Messrs. Vivien and Aulard.
Mons. Aulard—"De l'utilisation nationale des vineries provenant de la betterave ou de la melasse." Discussed by Messrs. Reviere, Effront, and Waller.
Mons. Aulard—"De la desiccation des mouts epuises (dreches) de brasserie ou de distillerie."
Mons. Egrot—"La diffusion simplifiee pour distilleries agricoles de betteraves, systeme Guillaume, Egrot, et Grange."
Mons. Millet—"Procédé de fermentation continue, sans coupages, systeme Guillaume, Egrot, et Grange." Discussed by MM. Mestre and Guillaume.

Mons. Mariller—"Sterilisation et pasteurisation des mouts en distillerie."

In the absence of the Authors, the following Papers were taken as read:—

- M. J. Marsellac—"Addition to the Coffey Still of a Guillaume column for the Epuration of Aldehydes."
M. L. Millet—"Un nouvel appareil pour la production d'alcool a haut degre."
Dott. G. Garbarini—"Separazione degli oli amilici ad alto grado di concentrazione e purezza, applicato a qualunque tipo di apparecchio di distillazione o rettificazione."
Herr E. Bauer—"Einige die Qualitat des Alcohol beeinflussende und charakterisierende Bestandteile."
Herr E. Bauer—"Ursache der Kali-Verluste bei der Verbrennung von Melassenschlempe."
M. T. Vidal—"Le travail en distillerie de la betterave cultivee sur terrains marecageux."

SECTION VII.—Agricultural Chemistry.

Morning Meeting: President, Dr. J. A. VOELCKER.

- Hall and Miller—"Production of Acids and Alkalis in the Soil." Discussed by Dr. Leather, Prof. Prianchnikov, and Messrs. Pouget, Kellner, and Hutchinson.
Leclerc and Breazeale—"Plant Food removed from Growing Plants by Rain or Dew." Discussed by Messrs. Huston, Leather, Hall, and Crowther.
Dojarenks (communicated by Prof. Prianchnikov)—"Wurzelauscheidung." Discussed by Messrs. von Feilitzen and Prianchnikov.
Leather—"Transpiration of Water by Plants in the Tropics." Discussed by Mr. Huston.
Leather—"Loss of Water from Soils in Dry Weather." Discussed by Dr. Pickering.
Afternoon Meeting:—President, Prof. MENOZZI.
Berry—"The Losses of Manurial Constituents in, and the Action of Preservatives on, Farmyard Manure during Storage." Discussed by Messrs. Hall, Hendrick, and Voelcker.
Voss—"Discovery of Phosphates in the Pacific." Discussed by Messrs. Hall and Voelcker.

SECTION VIII.a.—Hygiene.

The proceedings opened with the delivery of the Presidential Address, entitled "Sewage Disposal and Disinfection," by Sir JAMES CRICHTON-BROWNE, F.R.S.

A vote of thanks, proposed by Prof. H. R. KENWARD, and seconded by Dr. NICLOUX, of Paris, was carried with acclamation.

The following papers were then communicated:—

- Dr. Beunat—"La sterilization des Eaux par l'ozone a Nice."
Van der Made—"De la sterilization industrielle des Eaux potables en France." (In the absence of the author this paper was read by Dr. Rideal).
Dr. Sanna—"Le sterilizzazione delle acque Potabili mediante l'ozono."
Dr. Thresh—"Purification of Water for Potable purposes by means of Chlorine and Hypochlorite."
M. Dienert—"Etude critique des moyens employés pour apprecier la qualite des eaux potables."

SECTION VIII.b.—Pharmaceutical Chemistry.

The President, N. H. MARTIN, Esq., F.R.S.E. delivered an opening Address.

- Dr. K. Dieterich—"Ueber die Bestandteile und Verwertbarkeit der Paraguay Susspflanze Eupatorium Rebaudanum."
M. Leger—"Sur l'hordenine, alcalvide retire des touraillons d'orge."
Prof. Dr. H. Thoms—"Ueber Matico-Blatter und Matico-Oele."
Mr. E. M. Holmes—"Necessity for the Application of Botanical Knowledge to the Chemical Investigation of Plants."

Prof. A. Berg—"Sur l'elaterine."
Dr. F. von Konek-Norwall—"Ueber Thioderivate des Homoantipyryns" was postponed on account of the absence of the author.

SECTION VIII.c.—Bromatology.

The following papers were communicated :—
"Systems in Force for the Control of the Food Supply" :
In America, by Dr. Wiley ; France, by Dr. Ronn and Dr. Bordes ; Great Britain, by Dr. Buchanan.

SECTION IX.—Photo-Chemistry Photography.

After the delivery of the opening Address by the President of the Section, Sir W. de W. ABNEY, K.C.B., F.R.S., &c., the following papers were communicated :—

A. and L. Lumiere and A. Seyewetz—"Comparative Study of the Reducing Power of the principal Organic Developers, and of the means of Increasing or Reducing the Contrasts of the Developed Image."

Prof. R. Namias—"Influence de l'addition de fortes quantites d'acide borique sur la conservation et sur les proprietes du bain revelateur au diamidophenol."

Prof. R. Namias—"Recherches analytiques sur l'alteration du sulfite en presence de differents revelateurs et d'autres substances qui peuvent entrer dans les bains developpeurs."

L. P. Clerc—"On the Photographic Properties of Pyramidol."

"Subsequent Changes of the Developed Image, &c." :—
Prof. R. Namias—"Observations sur les bains de virage a l'or avec sulfuree."

Prof. R. Namias—"Substitution de composés de plomb et d'autres metaux a l'argent des images sur plaques ou films au gelatino-bromure et au chloro-bromure, et utilisation de ces composés comme mordants pour l'obtention d'images en differentes couleurs."

J. Hertzbergs—"Die Wirkungsweise des Ammoniumpersulfats."

L. H. Friedburg—"Photographic Demonstration of Light absorption."

SECTION XI.—Law, Political Economy, and Legislation affecting Chemical Industry.

The proceedings opened with the delivery of the opening Address by The Right Hon. Lord ALVERSTONE, the Lord Chief Justice of England.

The following papers were then communicated :—

Lord Justice Fletcher Moulton—"Some Fundamental difficulties in the Application of Law to Chemistry."

Justizrat Dr. E. Katz—"Über den Ausführungszwang."

A. J. Walter, Esq., K.C.—"Compulsory Working of Patents under §27 of the Patents Act of 1907."

Herr W. Boehm—"Compulsory Working of Patents."

Herr Doktor Osterriech—"Compulsory Working."

M. M. A. Husson—"Execution a l'etranger des jugements de condamnation pour contrefaçon."

Hugh Moulton, Esq.—"Subject-matter for Chemical Patents."

The following motion was carried :—

Proposed by Dr. SCHWEITZER, seconded by Dr. DAY and Dr. ECHARDT :—"That the Committees of the various countries party to the International Convention for the Protection of Industrial Property be requested to consider the desirability of adopting the following provision : 'The manufacture in one country of the Union protects the patentee against the revocation of his patent in all countries of the Union.'"

On Saturday, May 29th, the papers read in the different Sections were :—

SECTION I.—Analytical Chemistry.

Percy H. Walker—"Contracts Laboratory of the Bureau of Chemistry." "Contributions from the Laboratories of the General Chemical Company of New York."

Raimond Caramelli—"Analisi materie tartariche—Ricerca del piombo nell'acido tartarico e citrico."

Oscar Tobler—"Analisi materie tartariche—Ricerca del piombo nell'acido tartarico e citrico."

P. Carles—"Des Lies et Tartres ; Prises d'échantillons."

Paul Dutoit—"L'analyse physico-chimique des vins."

Falciola and Corridi—"Sulla determinazione del tannino nei liquidi concianti mediante l'impiego del refrattometro ad immersione di Zeiss."

Wilhelm Lenz—"Eine neue mikrochemische Unterscheidung der Roggen von Weizenstarke."

W. M. Gardner and H. H. Hodgson—"Action of Iodine on Phenols, with special reference to a Rapid Method for the Estimation of Tannin Matters."

Robert Clauser—"Ein heitliche Adjustierung von Messgefassen."

SECTION II.—Inorganic Chemistry and Allied Industries.

B. Lepsius—"Einfluss der Elektrolyse auf die Alkali Industrie."

H. Forster Morley—"Volumes of Chemistry in the International Catalogue of Scientific Literature." Discussed by Dr. McLeod and Sir Alex. Pedler.

C. Matignon—"Proprietes des Chlorures des metaux rares." Discussed by Prof. Ruff.

M. Z. Jovitchich—"Ueber die Löslichkeit von Oxyden der Elemente der Chromgruppe a propos eines neuen in Serbien entdeckten Chromminerals."

R. Salvadori—"Combinazioni complesse del Cobalto con gli acidi clorico e perclorico."

P. Fruchot—"Le grillage des pyrites dans les fours mecanique."

A. Bernthsen—"Ueber Luft Salpetersaure."

N. Caro—"Industrien des Kalkstickstoffs und verwandter Verfahren."

SECTION III.a.—Metallurgy and Mining.

M. Chaplet (France)—"Les alliages ferro-metalliques."

J. E. Stead, F.R.S. (Middlesbrough)—"Alloys of Iron, Carbon, and Phosphorus."

Prof. C. R. Namias (Milan)—"Malleable Cast-iron."

L. Guillet (France)—"Les aciers speciaux actuellement utilises."

Leon Guillet (Paris)—"Traitements thermiques des produits siderurgiques."

A. C. J. Charlier (London)—"Action of Hydrogen, Nitrogen, and other Gases on Metals, particularly Iron and Steel."

Nikolaus Gutowsky (Tomsch)—"Ueber den Zustandsdiagramm der Eisenkohlenstoff Legierungen."

SECTION III.b.—Explosives.

The President, Col. C. VITALI (Italy), on taking the chair, made the following remarks :—"Puisque j'ai l'honneur de prendre la precedence du jour a la suite de cette grande autorite sur les explosifs, Sir Andrew Noble ; il me semble que mon premier devoir est d'interpreter vos sentiments en lui envoyant vos plus vifs remerciements d'avoir bien voulu se soumettre a la fatigue, non seulement de nous presider, mais aussi de nous mettre par sa brillante conference au courant de ses derniers travaux scientifiques sur les explosifs de guerre."

Arthur M. Comey—"Study of the Velocity of Detonation."

Prof. Alexis Sapojenikow—"La theorie de nitration de la cellulose."

G. W. Macdonald—"Analysis of Sample of Gun-cotton manufactured at Faversham in 1847."

C. E. Bichel—"Neuerung bei der Anlage von Sprengstoff-fabriken." "Note sur quelques travaux executes au Siege d'experiences de Frameries (Belgique) depuis le congres de Rome."

SECTION IV.a (1).—Organic Chemistry and Allied Industries.

M. Wildermann—"Technical Process for Improvement of Low and Medium Grade Rubbers."

- H. Wichelhaus—"Derivate der Cellulose."
Prof. Vieweg—"Ueber Cellulose."
Julius Hubner and F. Teltcher—"Action of Caustic Soda-lye on Cotton."
Julius Hubner—"Effect of the Addition of Salt to the Caustic Soda-lye used in Mercerising."
Carl G. Schwalbe—"Die Chemie der Pflanzenfaser."
E. Knecht—"Action of Oxalic Acid on Cellulose."
L. Barthe—"Sur des phosphates aminomagnésiens."
"Sur le méthylarsinate d'antimoine."

SECTION IV.a (2).—*Physiological Chemistry and Pharmacology.*

(Joint meeting with Section VI.b.—Fermentation).

- A. Harden and W. J. Young—"Cell-free Alcoholic Fermentation."
W. M. Bayliss—"Colloidal Properties of Dye-stuffs."
B. Moore—"Hæmolytic Action of various Substances and a Hæmolytic Paradox."
A. R. Ling—"Determination of the Catalytic Power of Malt."
O. Rosenheim—"Sphaerorotation."
N. A. Barbieri—"Specimens of Products Isolated from Egg-yolk, Nervous Tissue, Bile."
A. Etard—"Specimens of Products from Albumins and Chlorophyll."
H. Steudel—"Specimens of Nucleic Acids and their Decomposition Products."
S. B. Schryver—"Influence of Adsorption Phenomena on the Synthesis of Complex Proteins."
R. H. Plimmer and R. Kaya—"Estimation of Phosphorus by Neumann's Method."
G. A. Buckmaster—"Oxidation of Guaiaconic Acid by Colloidal Metals—Bredig's Inorganic Ferments."
B. Moore and E. Whitley—"Effects of Removal of Peroxide upon Oxidase Tests."
A. R. Cushny—"Method of Investigating the Action of the Heart."
H. H. Dale and W. E. Dixon—"Action of Amines on the Blood Pressure."
E. H. Starling and W. M. Bayliss—"Production of Pancreatic Juice by Secretin."
J. Barcroft—"Method of Blood-gas Analysis."
A. Sator—(1). "Rate of Alcoholic Fermentation by Living Yeast." (2) "Intermediate Products in Alcoholic Fermentation."
G. Ciamician e C. Ravenna—"Sintesi della Salicina per mezzo delle Piante."
J. Wolff—"Peroxidases et oxydases artificielles; leurs rapports avec les diastases oxydants naturelles."
De Stocklin—"Sur quelques nouvelles reactions catalytiques oxydantes provoquées par certains combinaisons organiques de fer."
G. A. Buckmaster—"Guaiacum-peroxide reactions of Hæmoglobin, Hæmin, and Hæmatoporphyrin."
A. Guinsberg—"Die chemische Vorgänge bei der Kumyss- und Kefir-gärung."

SECTION IV.b.—*Colouring Matters and their Application.* (Technology of Textile Fabrics).

- L. Baumann and G. Thesmax—"Sur l'hydrosulfite de soude-formaldehyde et ses applications à l'impression."
P. Sisley—"Alterations des soies teintées, origine des accidents et moyens de les prévenir."
T. Valette—"Influence des produits employés dans le dégraissage et le blanchiment de la laine sur l'intensité et la solidité des couleurs teintées."
E. Agostini—"Sur l'emploi des savor's insolubles dans le traitement des fils et des tissus."
A. Scheurer—"Vaporisation des tissus."
F. König—"Ueber Pelzfarberei."
P. Heermann—"Das Blauholz und seine sekundären Funktionen."
S. von Kapff—"Ueber den Einfluss des Färbens auf die Eigenschaften der Wolle."
H. Lange—"Stuckfarberei."

SECTION V.—*Industry and Chemistry of Sugar.*

- Sir Daniel Morris—"Recent Researches in the Production of Seedling Sugar Canes in the West Indies."
Francois Strohmer (Vienna)—"Gibt es in der Zuckerrube optisch aktiven Nichtzucker welche die Polarisationsresultate beeinflussen?"
H. Pellet—"De l'influence des substances pectiques sur le dosage du sucre dans le betterave par les methodes du Dr. Zcheye et de MM. F. Strohmer and O. Fal-lada."
Francois Sachs (Brussels)—"Analyse des cossettes fraîches de betterave."
H. Pellet—"Dosage du sucre cristallisable dans la betterave."

On the motion of Prof. HERZFELD, a Committee, consisting of Messrs. Pellet, Sachs, Strohmer, Herles, Saillard, and Herzfeld, was appointed for drawing up the text of a proposition to be put before the International Commission for Unification of Sugar Analyses for making the aqueous method of Pellet for the analysis of beet the standard one.

- Hugh Main—"Estimation of Ash in Sugar-house Syrups by Determination of Electrical Conductivity."
J. D. Kobus (Java)—"Cane Seedlings in Java" (illustrated by lantern slides).
Henri Pellet (Paris)—"Sur les pertes en Sucrerie de Betteraves: et Sur les pertes en Sucrerie des Canes."
F. Herles (Prague)—"Ueber die optisch aktiven, der Einwirkung des Kalkes in der Wärme unterliegenden Nichtzuckerstoffen und über die Bestimmung ihrer Polarisation."
F. Ehrlich (Berlin)—"Ueber die Darstellung und Konstitution des Karamels und seine Bestimmung in Zuckersäften und Sirupen."
Auguste Aulard (Brussels)—(a) "Sur le phenomene osmotique qui s'accomplit durant l'extraction du jus de betterave par diffusion ou ébouillement." (b) "Du traitement du jus de betterave par l'acide sulfureux gazeux." (c) "Emploi de l'acide sulfureux liquide dans l'industrie sucrière." (d) "Filtration sur le sable du jus de diffusion et des divers produits de la sucrerie de betterave."
H. Decluy (Paris)—"Contribution à la théorie des fours à chaux, tables pratiques donnant la richesse en acides carboniques des gaz, emploi dans les fours à chaux des cokes d'usines à gaz."
Francois Dupont (Paris)—"Aire de culture de la betterave à sucre."

SECTION VI.a—*Starch Industry.*

- L. Vuafart—"Sur la composition minerale des blés et des farines."
F. Marion—"Des modifications subies par les farines avec l'âge."
R. Whympier—"Microscopical Study of Changes occurring in Starch Granules during Germination of Wheat. The Effect of Mineral Acids, Enzymes, and Heat on Granules of various Starches."
Geheimrat L. G. von Cramm—"The Use of Russian Corn for the Manufacture of Starch, Glucose, &c."
C. C. More—"Cassava: a Raw Material for Manufacture into Starch, Glucose, and Industrial Alcohol."

The last two papers were read by the representatives of the Russian and United States Governments, and were communicated with the object of bringing to the notice of British manufacturers the respective advantages of maize and cassava as a source of starch.

SECTION VI.b.—*Fermentation.*

- Dr. H. Lange—"Die Gärührung in Spiritusbrennereien und Presshefefabriken."
Docteur J. Effront—"Sur l'utilisation des résidus de distillerie."
G. Gimel—"Influence de quelques sels minéraux et en particulier du chlorure stanneux sur la fermentation."

- Dr. O. Mohr—"Hochkarburiert Spiritus als Motor treibstoff."
 E. Barbet—"L'industrialisation de la fermentation des vins; organisation de vineries à fermentation pure."
 Fr. Malvezin—"Sur le filtrage frigorifique."
 M. Rosenblatt—"Sur l'influence paralysante exercée par certains acides sur la fermentation alcoolique."
 E. Bauer—"Einige die Qualität des Alcohol beeinflussende und charakterisierende Bestandteile."
 E. Bauer—"Ursache der Kali-Verluste bei der Verbrennung von Melassenschlempe."

SECTION VI.b.—*Fermentation.*

Joint meeting of Sections IV.a bis and VI.b at the Institute of Physiology, University College, by invitation of Prof. Starling.

The meeting opened with a demonstration in the lecture theatre by Drs. Harden and Young on "Cell-free Alcoholic Fermentation in the Presence of Phosphates."

- Dr. Stator—"Rate of Alcoholic Fermentation by Living Yeast." "Intermediate Products in Alcoholic Fermentation."
 Dott. Ciamician and Dott. Ravenna—"Sintesi della Salicina per mezzo della Pianta."
 Dr. Wolff—"Peroxydases et oxydases artificielles."
 Dr. de Stocclin—"Sur quelques nouvelles reactions catalytiques oxydantes."
 Prof. Ginzberg—"Die Chemische Vorgänge bei der Kumys und Kefir Gärung."

During the morning the following demonstrations were given:—

- Prof. H. van Laer—"Determination of the Catalytic Power of Malt."
 Prof. Adrian J. Brown—"The Semi-permeable Properties of the Barleycorn."
 Dr. F. L. Usher—"Production of Formaldehyde by Light, in the presence of Chlorophyll."
 Prof. Dr. L. Marchlewski—"Spectra of Chlorophyll Derivatives."
 A. R. Ling—"Volumetric Determination of Reducing Sugars."
 Dr. G. A. Buckmaster—"Guaiacum-peroxide Reactions of Hæmoglobin, Hæmin, and Hæmatoporphyrin."

SECTION VII.—*Agricultural Chemistry.*

(Joint Session with Sections I., II., III.b, IV.a, and X.).

- Prof. Prianchnikov—"Sur le cyanamide de Calcium et le Dicyandiamide."
 Prof. von Feibitzen—"New Nitrogen Manures."
 Prof. Giuliani—"Des nouveaux engrais azotés utilisant l'azote atmosphérique."
 Prof. Riecke—"Lime Nitrogen, or Nitrolime, as the Nutritive Element of Plant Life; its Transformation in the Soil and its effect on various Crops."
 Prof. Perotti—"Azoto cianamidico nel terreno agrario."

(Joint Session with Sections I., II., III., IV.a, and X.).

Lecture on "Oxidation of Atmospheric Nitrogen."

SECTION VIII.a.—*Hygiene.*

- Dr. Schryver—"Physico-chemical Methods for Determining the Antiseptic Value of Disinfectants."
 Dr. Rideal and R. Orchard—"Suggested Improvements in Disinfectant Testing."
 Dr. Croner (Berlin)—"Ueber die Desinfektionskraft der wasserstoff superoxyds unter verschiedenen chemischen und Physikalischen Bedingungen."
 Dr. Thevenaz and H. Cade—"Standardising of Disinfectants."
 M. Wynter Blyth—"Chemical Control of Disinfectants."
 Georges Claudet—"Appareil de Sauvetage à Oxygene Liquide."
 M. Henriet—"Sur l'origine de l'ozone atmosferique." "La viciation de l'air des villes et de l'air confine—Causes et mécanisme des phénomènes observés."

- M. Nichoux—"Sur le rôle que jouent dans l'air atmosphérique les traces d'oxyde de carbone."
 MM. Ozier and Kohn-Abrest—"Dosages des petites quantités d'oxyde de carbone dans l'air."
 M. Frenkel—"Sur la desodorisation des gaz d'échappement des moteurs d'automobiles."
 Mr. Thomson—"Amount of Metabolism produced by the Breathing of Town and Country Air, &c., as increased by Carbonic Acid Gas in the Expired Air from the Lungs."

SECTION VIII.b.—*Pharmaceutical Chemistry.*

- Dr. W. H. Martindale—"Organic Arsenic Compounds."
 Dr. E. Maniell—"Azione fisiologica dell'acido para iodo fenilarsinico e di alcuni suoi derivati."
 Dr. Maniell—"Sull'aziphyll."
 M. Leger—"Essai des huiles simple intéressant spécialement la pharmacie."
 Dr. W. Lenz—"Eine mikrochemische Unterscheidung zwischen Roggen und Weizenstarke."
 M. G. Deniges—"Nouveaux procédés microchimique pour la caractérisation de l'arsenic et du phosphore en médecine légale."
 M. G. Deniges—"Réactions glyoxaliques des alcaloïdes de l'opium."
 Dr. Maniell—"Sa un nuovo derivato della cubebina; l'etere isocubebnico."
 Dr. S. Seidman—"Tallianine (terpene ozoné) et son emploi dans l'art vétérinaire et dans la médecine humaine."
 M. Fourneau—"Des anesthésiques locaux."
 Dr. Maniell—"Sull'guaiacol e sua azione curative."

SECTION VIII.c.—*Bromatology.*

- M. Andre—"Les méthodes d'analyse des denrées alimentaires en général."
 Prof. Piutti—"Unification of Analytical Methods."
 M. Wauters—"Unification internationale des méthodes d'analyse du beurre."
 M. Buchka—"Unification internationale des méthodes d'analyse des vins."
 M. Mastbaum—"Unification internationale des méthodes d'analyse des spiritueux."
 M. Vandervelde—"Unification internationale des méthodes d'analyse du lait."
 M. Lavalles—"Les limites dans les eaux potables."
 Dr. Wiley—"On the Methods employed in the United States."

SECTION X.—*Electro-chemistry and Physical Chemistry.*

- E. R. Taylor—"National and International Conservation of Water-power."
 M. Bodenstein—"Combination of Nitric Oxide and Oxygen."
 A. Rosenheim—"Electroreduction der Wolframsäure."
 Prof. Bernthsen—"Oxidation of Atmospheric Nitrogen" (with Experimental Demonstration).
 Prof. Birkeland—"Oxidation of Atmospheric Nitrogen."
 N. Card—"Industrien der Kalkstickstoffs und verwandter verfahren."

SECTION XI.—*Law, Political Economy, and Legislation affecting Chemical Industry.*

- Dr. Gustav Bokor—"Chemical Industry in Hungary."
 T. Bonnet—"Registration as a Trade Mark of the Scientific Name given by the Inventor to any New Pharmaceutical Product which has been announced."
 E. Fourneau—"Trade Marks in Pharmacy." "Pharmaceutical Products and French Law."
 Dr. H. Isay—"International Patents and the Paris Convention."
 E. de Laire—"International Patents."
 W. Jago—"Scientific Text-books as Evidence in Courts of Law."

The following Resolutions were proposed:—

Dr. BOKOR—"That each succeeding Congress of Applied Chemistry do examine and report upon the progress and position of chemical industry in each of the countries party to the Congress, having particular regard to the country in which the Congress is for the time being held, and to the relation between the development of chemical industry and customs tariffs."

Mons. E. FOUREAU—"That it is necessary that a fancy name designating a medicinal compound of definite composition should be protected as a trade mark as securely as such a name applied to a secret remedy or a remedy of indefinite composition."

Mons. E. FOUREAU—"That the Congress deprecates any patent legislation limiting the patentability of pharmaceutical products."

Dr. ISAY—"To commit the question of international acknowledgment of the right of prior use within the States adhering to the International Convention to the International Association for the protection of industrial property for further considerations."

"The Section thanks M. de Laire for an interesting and important paper on "The International Patent," and recommends this question to the attention of the International Association for the Protection of Industrial Property and to the National Committees for study with a view to future Congresses."

COPPER AS A REDUCING AGENT FOR FERRIC SALTS PREVIOUS TO THEIR ESTIMATION VOLUMETRICALLY.

By W. COLET BIRCH, B.A., A.I.C.

THE method of reducing ferric salts by means of granulated zinc has the disadvantage that filtering is necessary owing to the fine particles which become detached from the bulk of the metal. This causes loss of time, and, especially when dealing with hydrochloric acid solutions, danger of re-oxidation as the solution runs through the filter.

The following paper contains an account of an endeavour to apply thin sheet copper or copper-foil as the reducing agent; the reaction being thus $\text{Cu} + \text{Fe}_2(\text{SO}_4)_3 = \text{CuSO}_4 + 2\text{FeSO}_4$. The process claims to be advantageous both as regards saving of time and saving of material.

The copper only dissolves in an amount proportional to the iron present, so that the same copper can be used over and over again till it is quite thin, and shows a tendency to fray at the edges; when this takes place it should be discarded.

The method of working is as follows:—About twenty-five to thirty pieces of sheet copper, which should be as pure as possible—that described as "pure electrolytic" is best—of approximate dimensions 2 by 2½ cm. are placed in a round-bottomed flask, and washed, first with dilute nitric and then with dilute sulphuric acid.

The acid solution of the ferric salt is then added, and the whole gently boiled. If an ordinary flask is used the copper is liable to become matted at the bottom and cause explosive boiling.

For the same reason it is well to bend each piece of copper at right angles in the middle. Five minutes boiling is ample for the reduction; less than four is apt to give low results.

When the reduction is complete the flask is cooled under the tap, and the solution poured into a fresh flask; the copper is rinsed three times with distilled water, the washings added to the main quantity, and the whole titrated. A convenient thickness for the copper-foil is such that 100 sq. cm. weigh about 6 grms.

After the greater part of the necessary work had been completed, a paper by Storch was found (*Ber. d. Osterr.*

Gas. z. Förder. d. Chem. Ind., 1893, xv., 9), in which the use of copper as a reducing agent for ferric salts in presence of sulphuric acid was shown to be of practical value. What follows confirms Storch's experiments, and extends the process to hydrochloric acid solutions as well.

I. Reduction in presence of Sulphuric Acid.

(a) *With Copper*.—Twenty cc. of a solution of iron alum were boiled with dilute sulphuric acid and copper for five minutes, and then titrated with potassium dichromate, the ordinary ferricyanide indicator being used to ascertain the end-point.

	Cc. $\text{K}_2\text{Cr}_2\text{O}_7$ required (1 cc. = 0.005482 grm.).	
Air-free water for washing the copper..	13.02	13.07
Unboiled distilled water for washing ..	13.03	12.95
Dilute H_2SO_4 for washing	12.96	—
(Mean = 13.00 cc.).		

Twenty cc. of the same iron solution when reduced with copper and titrated with permanganate required the following:—

	Cc. K_2MnO_8 required.			
Unboiled water for washing..	13.63	13.54	13.54	13.62
(Mean = 13.58 cc.).				

These 13.58 cc. of the permanganate solution are equivalent in oxidising power to 12.93 cc. of the dichromate solution used in the first series of titrations.

(b) *With Zinc*.—Twenty cc. of the ferric solution after reduction with zinc and sulphuric acid in the usual way require:—

Cc. permanganate (1 cc. = 0.003331 grm.)	13.68
	13.71
Mean	13.69
Calculated as $\text{K}_2\text{Cr}_2\text{O}_7$..	12.90
Cc. permanganate (1 cc. = 0.003306 grm.)	13.82
	13.99
Mean	13.03
Calculated as $\text{K}_2\text{Cr}_2\text{O}_7$..	13.03
Mean	12.

II. Reduction with Copper in presence of Hydrochloric Acid.

(a) *Preliminary*.—The reaction which takes place is $\text{FeCl}_3 + \text{Cu} = \text{FeCl}_2 + \text{CuCl}$. Since ferrous chloride and cuprous chloride are produced in equivalent proportions, twice as much dichromate should be required for the same amount of iron as in the case when sulphuric acid alone is present. The presence of cuprous chloride necessitates care being taken to prevent oxidation during cooling and titration.

It was found sufficient to drop a small piece of marble, or better calcite, into the flask while the solution was being cooled, and another piece into the titration flask. The copper is washed with dilute hydrochloric acid, both the washing and titration being carried out as expeditiously as possible.

At first numbers were found which were considerably smaller than the theoretical double of those obtained when sulphuric acid alone was present.

It was found, however, that the method of using the ferricyanide indicator had a certain influence on the end-points, the presence of hydrochloric acid and copper tending to hinder the formation of the blue colour.

Table I. shows the results obtained under varying conditions.

The solution titrated consisted of ferrous sulphate, to which had been added enough copper sulphate to render the amount of copper present approximately the same as

TABLE I.—*Influence of Indicator on the End-point.*

Condition of indicator.	Condition of iron solution.	Cc. $K_2Cr_2O_7$ required.					Mean.
Saturated water solution.	Dilute H_2SO_4 ; no copper.	13.59	13.58	13.64	13.58	13.64	13.60
Saturated water solution.	15 cc. HCl (1 : 2); copper.	13.15	13.21	13.14	13.27	13.22	13.20
Saturated solution in HCl (1 : 2).	15 cc. HCl (1 : 2); copper.	13.25	13.30	13.21	13.38	13.30	13.28
Saturated solution in H_2SO_4 (1 : 3).	15 cc. HCl (1 : 2); copper.	13.26	13.28	13.30	13.41	13.32	13.31
Dilute water solution.	15 cc. HCl (1 : 2); copper.	13.23	13.15	13.11	—	—	13.16

NOTE.—The method of waiting half-a-minute to allow the reaction in the drop on the tile to complete itself was not used; this accounts for the numbers in lines 2, 3, 4, and 5 being lower than those in line 1 (see text).

TABLE II.—*Influence of the Amount of Hydrochloric Acid on the Reduction.*

(Volume of ferric solution 20 cc. in all cases).

Amount of HCl.	Cc. $K_2Cr_2O_7$ required		Mean.
5 cc. (1 : 2)	26.08	26.01	26.04
10 "	25.95	25.93	25.94
15 "	25.92	25.94	25.93
25 "	25.92	26.19	26.05
50 "	26.25	26.34	26.29
10 cc. (conc.)	26.30	26.29	26.29
25 "	27.49	28.18	27.83

TABLE III.—*Influence of the Amount of Sulphuric Acid on the Reduction.*

(Volume of ferric solution 20 cc. in all cases).

Amount of H ₂ SO ₄ .	Cc. KMnO ₄ required.		Mean.
20 cc. (1 : 8)	13'90	13'93	13'91
40 " "	13'89	14'04	13'96
20 cc. (1 : 4)	13'93	13'94	13'93
40 " "	13'95	13'99	13'97
20 cc. (1 : 2)	13'90	13'97	13'93
40 " "	13'95	13'97	13'96

NOTE.—The dichromate solution in Table II., and the permanganate solution in Table III., are not equivalent in their oxidising power, so that the numbers in Table III. are not intended to be half those in Table II.

TABLE IV.

	Reduction by zinc and H ₂ SO ₄ .	Reduction by Cu and H ₂ SO ₄ .	Reduction by Cu and H ₂ SO ₄ .	Reduction by Cu and HCl.
	Cc.	Cc.	Cc.	Cc.
K ₂ Cr ₂ O ₇ equivalent to the K ₂ Mn ₂ O ₈ used ..	12'96	12'93	—	—
K ₂ Cr ₂ O ₇ required	—	—	13'03	25'93
				K ₂ Cr ₂ O ₇ used by the iron only, 12'96.
Difference from value found by Zn	—	-0'03	+0'07	0'00

TABLE V.—*Iron in Spiegeleisen.*

Reducing agent.	Weight of metal.	$\text{K}_2\text{Mn}_2\text{O}_8$ (1 cc. = 0.00279 grm.).	Correc- tion.	Corrected value.	Mean.	Weight of iron.	Difference from mean.
	Grm.	Cc.	Cc.	Cc.	Cc.	Grm.	Grm.
Zn and H_2SO_4 ..	0.1486	20.05	0.17	19.88	19.89	0.09808	+ 0.00002
Cu and H_2SO_4 ..	0.1486	20.06	0.16	18.89			
	0.1486	20.04	0.16	19.88	19.88	0.09805	- 0.00001
				Mean	0.09806		

TABLE VI.—*Corrections for Impurities in Reagents.*

Permanganate required to produce permanent pink colour (cc.).

Blank experiments with Zn and H ₂ SO ₄		0.18	0.11	0.19	0.19	Mean.
Blank experiments with Cu and H ₂ SO ₄		0.21	0.14	0.11	0.18	0.17
						0.16

TABLE VII.—*Iron in Hæmatite.*

Reducing agent.	Weight of hæmatite. Grm.	Permanganate (1 cc. = 0·00279 grm.). Cc.	Correction. Cc.	Corrected value. Cc.	Mean. Cc.	Weight of iron. Grm.	Difference from mean.
Zn and H ₂ SO ₄ ..	0·2475 0·2475 0·2475	31·04 31·00 30·94	0·17	30·87 30·83 30·77	30·82	0·1520	+0·0001
Cu and H ₂ SO ₄ ..	0·2475 0·2475	30·83 31·16	0·16	30·67 31·00	30·83	0·1520	+0·0001
Dichromate (1 cc. = 0·003722 grm.).							
Cu and HCl. ..	0·2475 0·2475 0·2475	71·45 71·49 71·60			71·51	0·1515	-0·0004
Gravimetrically ..	0·3418	Fe ₂ O ₃ found = 0·3006 grm.; therefore weight of iron in 0·2475 grm. ore =					0·1522
				Mean		0·1519	+0·0003

TABLE VIII.—*Spathic Iron Ore.*

Reducing agent	Weight of ore. Gm.	Permanganate (1 cc.=0.002797 grm.). Cc.	Cor- rection.(a)	Corrected value.	Mean. Cc.	Weight of iron. Gm.	Difference from mean.
Zn and H ₂ SO ₄ ..	0.1078	7.97	0.19	7.78	7.80	0.03855	+0.00009
	0.1078	7.98		7.79			
	0.1078	8.04		7.85			
Cu and H ₂ SO ₄ ..	0.1098	7.88	0.13	7.75	7.76	0.03836	-0.00010
	0.1078	7.90		7.77			
	0.1078	7.90		7.77			
SO ₂	0.1078	7.78			7.78	0.03846	—
	0.1078	7.78					
K ₂ Cr ₂ O ₇ (1 cc.=0.003884 grm.).							
Cu and HCl. ..	0.1078	17.51			17.42	0.03849	+0.00003
	0.1078	17.35					
	0.1078	17.42					
Mean						0.03846	

(a) A different correction, owing to the use of different samples of zinc and copper.

would be met with in determining the amount of iron in a ferric solution.

The saturated acid solution of the indicator gives a higher value than the water solutions, and the end-point is more distinct.

The best method of obtaining the true end-point was found to be as follows:—

The indicator is a freshly prepared saturated solution of potassium ferricyanide in dilute sulphuric acid. A drop of the solution to be tested is mixed with the drop of indicator on a white tile, and if a blue colour is not immediately developed the drop is covered with a crucible to exclude light and dust, and allowed to stand for thirty seconds. If at the end of this time no blue colour is developed the titration is taken to be complete.

It is necessary to wait the full thirty seconds, because in the very dilute state of the ferrous salt the colour only appears slowly.

This method of procedure is unnecessary if the dichromate solution is standardised against known amounts of ferric iron, which are reduced with copper under conditions approximately similar to those which will obtain when an unknown amount of iron is being estimated. It should be mentioned, perhaps, that great care must be taken in dealing with hydrochloric acid solutions, that the copper is perfectly clean, and not superficially oxidised.

Unless this is so more cuprous chloride will be formed than is equivalent to the iron present, and a high result will be obtained.

The superficial layer of oxide is easily removed by boiling with dilute sulphuric acid and rapidly washing with distilled water. The iron solution to be reduced should then be added as quickly as possible.

(b) *Influence of Varying amounts of Acid on the Reduction.*—Table II. shows the effect of varying the amount of hydrochloric acid. To secure accurate results the amount of free acid must not be greater than 25 cc. of acid of strength 1 to 2.

Table III. contains a similar series of values obtained when sulphuric acid was used. The amount of acid has no effect on the value found.

(c) *Reduction of the Ferric Alum Solution.*—Twenty cc. of the iron solution, when boiled for five minutes with copper and 15 cc. of HCl solution (1 to 2), required—

Cc. K ₂ Cr ₂ O ₇ (1 cc. = 0.005482 gm.).					
Dilute HCl for washing	25.82	25.92	25.88	26.08	25.94
(Mean = 25.93).					

Table IV. contains a summary of the determinations of the iron solution for purposes of comparison. The numbers are the mean values of the previous determinations.

III. Estimation of Iron in Ores and Alloys.

(a) *Spiegeleisen.*—The material was dissolved in nitric acid. In order to destroy organic matter potassium chlorate was added, and the solution boiled. The iron was then precipitated with ammonia, washed till free from chlorides, and dissolved in sulphuric acid. The results obtained appear in Table V.

The corrections in the fourth column are for impurities in the zinc and copper. They were found by performing blank experiments, the details of which appear in Table VI.

(b) *Hamatite.*—The finely powdered specimen was dissolved by digesting with concentrated hydrochloric acid and a little potassium chlorate. The results obtained appear in Table VII.

The dichromate solution was standardised on re-crystallised ferrous ammonium sulphate, which was oxidised and then reduced with copper in presence of hydrochloric acid.

(c) *Spathic Iron Ore.*—The ore was dissolved by digesting with aqua regia. The results appear in Table VIII.

It appears therefore that copper provides a convenient and easily handled reducing agent for ferric salts previous to their estimation volumetrically, provided that the precautions noted above are taken.

My thanks are due to Mr. C. T. Heycock, King's College, for much advice and assistance during the course of the work.

King's College, Cambridge,
May, 1909.

THE QUANTITATIVE DETERMINATION OF NICKEL WITH DYMETHYLGLYOXIME AS APPLIED TO VARIOUS MATERIALS.

O. BRUNCK describes in the *Zeitschrift für angewandte Chemie*, 1907, xx., p. 834, a method for the quantitative determination of nickel with dimethylglyoxime. If a neutral solution of nickel salt be treated with an alcoholic solution of dimethylglyoxime a red crystalline precipitate is produced. The acid set free in the reaction, however, causes the precipitation to be incomplete, and it is necessary to add ammonia in order to get accurate results. The precipitate can be dried at temperatures above 100° C., without decomposition (it sublimes at 250° C.) and has the formula C₈H₁₄N₄O₄Ni. Cobalt does not interfere, provided that not more than 0.1 gm. per 100 cc. is present. In working the process, the neutral or faintly acid solution containing nickel is heated and treated with a slight excess of dimethylglyoxime. Ammonia is then added gradually

until a slight excess is present, the precipitate is collected in a Gooch crucible, washed with hot water, and dried for three-quarters of an hour at 110° — 120° C. If nickel and cobalt are both present, they are determined together by electrolysis, the deposit is dissolved in nitric acid, the solution evaporated with hydrochloric acid, and the nickel determined as described above.

Another article appeared by the same author in the *Zeitschrift für angewandte Chemie*, 1907, xx., pp. 1844—1850, on the quantitative determination of nickel in the presence of cobalt, zinc, manganese, iron, aluminium, and chromium, by means of dimethylglyoxime.

Nickel and Cobalt.—The conversion of nitrate into chlorides before precipitation is unnecessary. If more cobalt than nickel is present, a larger excess of dimethylglyoxime is required, and where the quantity of nickel is small, a method is used in which sodium-acetate replaces ammonia. In this case 0.5 gm. of the sample is dissolved in hydrochloric acid and the solution evaporated nearly to dryness. To the hot liquid after being diluted to 400 cc., are added 0.2 gm. of dimethylglyoxime and 2 grms. of sodium acetate, and the precipitate is filtered off after half an hour.

Nickel and Manganese.—Sodium acetate is used instead of ammonia to neutralise the mineral acid.

Nickel and Zinc.—The separation succeeds in the presence of ammonia or acetic acid, but the latter is preferable.

Nickel and Iron.—To the solution containing iron, in the ferric state, tartaric acid is added before precipitation, to prevent the subsequent formation of ferric hydroxide on adding ammonia. The method is applicable to nickel steels, since manganese does not interfere.

Nickel and Aluminium.—The method is similar to the "nickel and iron" method.

Nickel and Chromium.—Tartaric acid is added as above to prevent the precipitation of chromium by ammonia, but it is necessary to have a sufficiency of ammonium chloride present also. Nickel in nickel chrome steel may be thus directly determined.

The methods are very accurate and rapid; a determination requires one hour, and the somewhat costly reagent may be readily recovered from the precipitates.

H. Vdoviszewski publishes an article on "The Determination of Nickel in Nickel Steel and Nickel Chrome Steel by means of Dimethylglyoxime" in *Stahl und Eisen*, 1908, xxviii., p. 960, which is a modification of Brunck's method. The igniting of the precipitate is done in an ordinary platinum or porcelain crucible instead of using Gooch's crucible. The sublimation of the nickel oxime precipitate is prevented by careful manipulation. For the separation of nickel from iron Rothe's iron extraction method by means of an ether-acetone mixture is used. After the solution is freed from iron, the nickel is precipitated with the respective amount of a 1 per cent alcoholic dimethylglyoxime solution. In the presence of chromium 0.5 to 1 gm. of tartaric acid and an excess of ammonia is added to the solution before precipitation. The method requires about three hours and is very accurate. —*The Chemical Engineer*, ix., No. 4.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlviii., No. 15, April 13, 1909.

Study of Gases Disengaged by the Action of Cupric Salts on Steels.—E. Goutal.—When steel is attacked by slightly acid copper chloride or potassium chloride at a moderate temperature in a current of nitrogen a loss of carbon amounting to 0.01 to 0.05 per cent occurs.

The carbon is evolved in the form of gaseous compounds, CO, CO₂, &c. The loss is halved if the organic analysis of the carbonaceous residue is carried out without previous drying. Moreover, all loss is avoided if the cupric solution is boiled and the gases set free are passed over red-hot platinum in presence of excess of oxygen, and the carbon dioxide formed is received in baryta water.

No. 16, April 19, 1909.

Determination of Moisture in Altered Milks.—André Kling and Paul Roy.—The water in milk is generally determined by finding the percentage of dry residue after the fat has been extracted. This method is satisfactory for fresh milk, but when it is kept it undergoes changes owing to which the amount of dry residue varies progressively and shows a decided decrease. The total nitrogen, corresponding to the albumenoids of the milk, however, remains absolutely unaltered, and from the determination of this constituent it can be ascertained with certainty whether water has been added to the milk or not.

MEETINGS FOR THE WEEK.

MONDAY, 7th.—Royal Institution, 5. General Monthly Meeting.

TUESDAY, June 8th.—Royal Institution, 3. "Biological Chemistry," by F. Gowland Hopkins, F.R.S., &c.

WEDNESDAY, 9th.—Society of Public Analysts, 8. "Estimation of Iron by Permanganate in presence of Hydrochloric Acid," by G. C. Jones and J. H. Jeffery. "Jaffé's Colorimetric Method for the Estimation of Creatinine," by A. C. Chapman. "Estimation of the Alkalinity of Bleaching Powder Solutions," by K. J. P. Orton and W. J. Jones. "Sabatier-Senderens Test for distinguishing between Primary, Secondary, and Tertiary Alcohols" and "New Test for the Halogens," by G. B. Neave.

THURSDAY, 10th.—Royal Institution, 3. "A Modern Railway Problem—Steam v. Electricity," by Prof. W. E. Dalby.

FRIDAY, 11th.—Royal Institution, 9. "Problems of Helium and Radium," by Prof. Sir James Dewar, F.R.S., &c. Physical, 8. "The Arthur Wright Electrical Device for Evaluating Formulae and Solving Equations," by A. Russell and A. Wright. "The Echelon Spectroscope, its Secondary Action and the Structure of the Green Hg Line," by H. Stansfield. "Proposed International Unit of Candle Power," by C. C. Paterson. "Inductance and Resistance in Telephone and other Circuits," by J. W. Nicholson. "Terrestrial Magnetism," by G. W. Walker. "Form of the Pulses constituting White Light," by A. Eagle.

SATURDAY, 12th.—Royal Institution, 3. "The Vitality of Seeds and Plants," by F. F. Blackman, F.R.S., &c.

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CHEMICAL NEWS OFFICE.

16 NEWCASTLE ST., FARRINGTON ST., E.C.

THE CHEMICAL NEWS.

Vol XCIX., No. 2585.

SEVENTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

MONDAY, MAY 31st.

PROFESSOR O. N. WITT'S LECTURE.

In the afternoon a Lecture was delivered to the assembled Congress by Geh.-Rat. Prof. O. N. WITT on "Evolution in Applied Chemistry." He commenced by pointing out some of the relations existing between biology and applied chemistry. Evolution was no longer a working hypothesis of natural science; it had become a new way of thinking, a method of harvesting everlasting truth from the fleeting changes of passing life. It was not applicable to living plants and animals only, but to everything that was capable of growth and alteration and improvement. Why should not this method be extended to the study of human achievements, of science as a whole—why not to applied chemistry? England, which had given to all the other nations the invaluable gift of Evolution, was the classical soil on which an attempt might be made to apply it in a new manner. It might help them to understand the struggle for existence, which in chemistry and its applications was as rife as amongst the organisms of the deep sea or the tropical forest.

One of the best applications of empiricism and theory was the examination of old empirical industrial processes by the methods and in the light of modern chemical science. A great deal of valuable information had been obtained in this way; much more remained to be discovered. Who knew what a host of information might yet be lying dormant in unread Egyptian papyri and palimpsests! But we had living empiricism at our doors which we allowed to die and to sink into oblivion without attempting to study it and to learn the lesson it had to teach. This great treasure was the industrial experience of the Eastern nations. The people of Persia, India, China, Japan, Burma, Siam, Cambodia, and the innumerable islands of the Pacific, were possessed of methods for the treatment and utilisation of the products of Nature which were in many cases equal, if not superior, to our own. Those methods must be to a large extent based upon chemical principles. Was it not strange that we knew so little about them, and that little generally only indirectly through the accounts of travellers who were no chemists? If all these peculiar methods were fully known and described by persons who had seen them applied and watched their application with the eyes of a chemist, it would be of the greatest utility to our own industries. As instances of industries which had benefited by secrets derived from the East, he mentioned Turkey-red cotton-dyeing, calico-printing, and indigo-dyeing and porcelain.

These International Congresses, he said, ought to make it one of their important duties to watch over the intellectual wealth of the past, and to collect it before it disappeared for ever by reason of the adoption of the quicker Western methods. It would be strange indeed if we could not gather some acceptable hints from surveying the broad expanse of the human toil and thought of centuries.

A truth too often forgotten in our own times was that no industry, and especially no chemical industry, could be transplanted, such as it was, from the place in which it had been successfully developed, into any other, without having to undergo a complete change, which taxed to the utmost the organising and inventive power of those who made the attempt. There were frequent examples of manufacturers, who had risen to great prosperity, suffering enormously by transferring their business to some new locality. In many cases it was merely a move in their

own country, yet it meant generally a far-reaching adaptation to altered conditions. But if it became a question of transplanting a manufacture from one country into another, there would have to be a new creation if it were to be a success. It was the destiny of aquatic organisms to conquer land as a dwelling-place, and it was the destiny of the industrial countries of the present day to carry industry to the nations that were ready to receive it. Whenever an industry left its native country it had to be re-modelled to suit different conditions.

After citing many examples of the principles of economy which universally pervaded living nature, Prof. Witt asked whether these principles were not the very essence of all industrial chemistry. The history of applied chemistry, he said, was teeming with instances in which the survival of the fittest meant neither more nor less than a victory of economy. The closed ring of industrial chemical processes working in connection with Leblanc's method of producing soda, was practically extinct on the Continent, and materially reduced in its importance in England, because it was a wasteful process, wasteful in its utilisation of material, and wasteful in its consumption of energy. Taken as a whole, the progress of the chemical industry did not so much consist in the improvement of the apparatus as in the simplification of the fundamental chemical reactions. More than once a seemingly insignificant chemical alteration of an industrial process had produced an effect the same or better than the introduction of the most ingenious and costly plant.

It was not so very long since we had begun to have a conscience for fuel. We were now awake to the fact that the quantity of fuel required for an industrial process was very much dependent on the way in which it was made to do its work. A striking example of the transformation of our views about fuel and its proper use was the history of the smoke question. There was a time when smoke was considered a necessary evil, but after a while it began to be looked upon as a nuisance, and war was declared against it. But now we knew that smoke was a waste, and that nobody had better cause to wage war against it than he who produced it. A smoking chimney did not only carry visible unburned carbon into the atmosphere, but in nine cases out of ten also invisible carbonic oxide and methane with all the latent energy they contained. Smoking chimneys were thieves, and their misdeeds should not rise unavenged to heaven. Regenerative gas-heating was not only a sure prevention of smoke, but also the most powerful means of economising heat, and therefore one of the greatest acquisitions of modern industry. The saving of national wealth effected by it might amount to a sum sufficient to pay the aggregate national debts of all the civilised nations. Uncivilised nations were blessed with neither national debts nor heat-regenerating appliances.

The lecturer finally drew attention to the wonderful phenomena of symbiosis and aggregation. Symbiosis was of very frequent occurrence. Plants or animals of totally different nature and organisation, or even plants and animals, might combine for joint life and activity with the object of helping and protecting each other in the great struggle for existence. There was a great deal in human life and institutions, in morals, politics, and science, which reminded them that the human race, as an intrinsic part of animated nature, had also inherited its all-prevailing tendency for combining forces. The various forms of chemical industry were essentially symbiotic. They depended upon each other for their success and progress. Chemical works came in shoals if they came at all. (Laughter). The more varied and numerous the factories, the more they prospered, in spite of their complaints of growing competition. The congresses of chemists represented a modern form of symbiotic effort, which was the more remarkable because it was international. They proclaimed the great truth that science knew no boundaries and frontiers, that it was the joint property of all humanity, and that its adherents were ready to flock together from all parts of the world for mutual help and progress.

SECTIONAL PROCEEDINGS.

In continuation of our report last week we give below the titles of the papers read at the different sectional meetings. Arrangements have been made whereby the more important of the papers likely to interest our readers will be published in full or in abstract in the *CHEMICAL NEWS*.

MONDAY, MAY 31st.

SECTION I.—Analytical Chemistry.

At the Morning Meeting the following papers were communicated:—

- G. Chesneau—"Sur le dosage du phosphore dans les fers, fontes et aciers."
 Capitaine Nicolardot—(a) "Analyse de ferrosilicium." (b) "Sur la dénomination du Niobium ou Columbiun." (c) "Analyse du Wolfram et de la Hübnerite et séparation de l'acide tungstique d'avec la silice."
 Nicolardot and Krell—"Analyse des alliages d'antimoine."
 E. Goutal—"Etude des gaz dégagés par l'action des sels cuivriques sur les aciers (dosages du CO₂ et du CO)."
 G. T. Holloway—"Detection and Estimation of Rare Metals in Minerals, particularly of such as are used in (1) the Manufacture of Special Steels, and (2) of Incandescent Mantles."
 Henry Sand—"New Apparatus for the Rapid Electro-analytical Separation of Metals."
 M. Delachanal—"Analyse des gaz dissous dans les métaux."
 Paul Truchot—"Dosage du zinc dans les blendes et les pyrites." "Dosage du fluor dans les blendes." "Application de l'électrolyse au dosage du zinc dans les minerais de zinc et autres." "Discussion de la méthode de Schaffner. Dosage du fluor dans les blendes."
 Gaetano Maderna—"Sulla precipitazione dell'acido fosforico in presenza di acidi organici." "Sulla determinazione dello zolfo per via catalitica."
 Marco T. Lecco—"The detection of Mercury in Toxicological Analysis." "Disturbing effect of Alcohol in the detection of Volatile Poisons." "Determination of Lithium in Water."
 Olof Rodhe—"Principles of Economical Firing and an Apparatus for this purpose."

The afternoon meeting was opened by Dr. CONSTAM with a discussion on "Analytical Methods of Fuel Testing." He proposed the following general definition for the yield of volatile matter in fuels:—"The percentage which is found by subtracting from one hundred the yield of coke obtained, by the method of the American Committee on Coal Analysis (*Fourn. Am. Chem. Soc.*, xxi., p. 1122) from 1 grain of fuel in a bright platinum crucible. The yield must always be calculated upon the pure combustible matter."

The proposal was put to the meeting, and carried unanimously.

The following papers were then communicated:—

- Edward Gudeman—"Technical Coal Analysis."
 Prof. J. Sebelien—"Some Amendments in the Execution of the Kjeldahl Process for the Determination of Nitrogen."
 Dr. Collett—"Determination of Molybdenum."
 Andrea Sanna—"Apparechio per prendere il campione delle aqua profonde."
 A. Vila et R. Piperand—"Sur un procédé de séparation et du dosage du zinc."

SECTION II.—Inorganic Chemistry and Allied Industries.

The following papers were communicated:—

- D. Heintze—"Zur Geschichte der Erfindung des Porzellans durch Joh. Friedr. Böttger."
 A. Piutti—"L'elio nel Vesuvio e nell'ana di Napoli Minerali con elio senza genitori radio-attivi."

- G. Keppeler—"Giessverfahren in der Keramischen Industrie."
 L. Baraduc Muller—"Les Produits refractaires."
 S. Wologdine—"Conductibilité calorifique perméabilité et porosité des matériaux réfractaires."
 E. Kohn-Abrest—"Etude sur l'aluminium: procédé de l'analyse rapide de l'aluminium."
 G. Arrivant—"Sur les Arséniures de Manganese."
 G. Morselli—"Stato attuale dell'industria dei gas compressi in Italia."
 L. Oeconomides—"Die Chemische Industrie in Griechenland."
 A. Spiegel—"Manufacture of Ammonia from Carbonaceous Substances."
 G. Harker—"Fire Extinction and Disinfection in Ships and other Enclosed Spaces."
 J. Jacobsen—(1) "Quelques phosphates et arseniates doubles." (2) "Action de l'ammoniaque et de la pyridine sur des sels mercuriels."
 R. Fabiny—"Ueber Trass von Siebenbirgen."

SECTION III.a.—Metallurgy and Mining.

(Mining and Ore Treatment).

The following papers were communicated:—

- Robert H. Richards (U.S.A.)—"Study of some Laws of Concentrating Ores."
 M. Strap (Paris)—"Etat actuel des mines d'or francaises."
 J. B. Williams (Brazil)—"Chemistry of Alluvial Gold Mining."
 Prof. D. E. Pannain (Rome)—"La solubilità dell'argento e delle sue leghe nelle miscele di acidi."
 Prof. E. Hauser—"Un nouveau modele de grisoumetre."
 Dr. S. Icard (Marseille)—"Eclairage de mine-lamps de sureté."
 M. Katona (Budapest)—"Thermal Calculations in the Use of Gaseous Fuel in Blast-furnace Practice."
 Werner Cronquist—"Ferosilicon."
 M. Clausel de Coussergues (France)—"Etat actuel de l'electrosiderurgie."
 L. Revillon (Paris)—"Emploi industriel de la metallographie microscopique."
 Prof. R. Schelle (Selmechbanya)—"Darstellung von reinem tellur."
 M. Jarl (Copenhagen)—"Kryolith."
 P. Weiss (Zurich)—"Le ferromagnetisme et l'étude des métaux et alliages."

The adjourned discussion on M. Revillon's paper was now taken.

SECTION III.b.—Explosives. (Morning).

After a short opening Address by the Presidents, the following papers were communicated:—

- Maurice Jacque—"Influence of Micro-organisms and Vegetable Acids on the Stability of Nitric Esters (Nitro-cellulose, Nitro-glycerin, &c.)."
 J. Taffanel—"Les travaux de la station d'essais de Liévin."
 Prof. Chas. E. Munroe—"Development of Explosives in the United States during the last Three Years."
 Prof. R. Wolfenstein and Dr. Botes—"Ueber Nitrierung in Gegenwart von Quecksilber."
 G. W. Patterson—"Detection of Mercury in Explosives."
 Dr. Stephan P. Jannopoulos—"Nachweis von Sublimat in der Komprimierten Schiessbaumwolle."

Joint Meeting of Sections III.b and III.a. (Afternoon).

- V. Watteyne—"Compte rendu des travaux de la Commission Internationale pour l'étude de l'unification des méthodes d'épreuve sur la stabilité des explosifs."

Resolved—"That it is desirable that the International Commission appointed in Rome in 1906 to consider the standardisation of tests for the stability of explosives be re-appointed till the next Congress."

- Geh. Reg.-Rat. Prof. Dr. Mente—"Zur Untersuchung der Sprengstoffe auf Zundsicherheit in Schlagwettern und Kohlenstaub."
Geh. Rat. Prof. W. Will—"Zur Untersuchung der Sprengstoffe auf Zundsicherheit in Schlagwettern und Kohlenstaub."
Berg.-Ass.-Beyling—"Die Prüfung von Sicherheit von Sprengstoffen."
Louis Barthelemy—"Amorçage des Coups de Mines."
Prof. P. Phillips Bedson—"Experimental Demonstration of the Inflammability of Mixtures of Air and Coal-dust."

SECTION IV.a (1).—*Organic Chemistry and Allied Industries.* (Morning).

The following papers were communicated:—

- H. R. Procter—"The Structure of Organic Jellies."
V. Boulez—"Nouvelle methode d'analyse des huiles essentielles renfermant des alcools tertiaires." "Désagrégation de la molécule triglyceride dans les matieres grasses par saponification alcaline-aqueuse."
A. Haller and G. Bechamp—"Alcoolise de quelques ethers, sels et glycerides."
A. Haller and A. Brochet—"Action de l'ozone sur le ricinoleate de methyle."
J. Effront—"Nouvelle methode de fabrication d'acides gras."
J. B. Senderens—"Nouveau procede de fabrication industrielle des oxydes d'ethyle et de methyle."
Raicoff—"Ueber den Einfluss der Zusammen-setzung und Struktur organischer Säuren auf die Stabilität ihrer Karboxylgruppe bei hoher Temperatur."
Ch. Cofignier—"Peintures sousmarines et Peintures ignifuges." "Progres recents dans la fabrication d'acides gras."
P. Falcicola—"Sopora i sali d'ammonio dagli acidi grassi (oleico, palmitico e stearico) e sulla separazione dell'acido oleico dagli acidi grassi saturi."
S. Fachini—"L'olio di vinacciole." "L'olio di crisalido e la sua applicazione all'industria saponiera." "La biacca e i suoi surrogati." "I saponi marmorati e il fenomeno della marmoratura."

Joint Meeting of Sections IV.a (1) and IV.b. (Afternoon).

The following papers on "Fluorescence and Colour in Relation to Chemical Constitution" were communicated:—

- H. Kauffmann—"Valenz und Fluorescenz."
A. G. Green—"Constitution of the Salts of the Phthaleins and the Cause of Colour in the Triphenylmethane Series."
H. Ley—"Beziehung Zwischen Fluorescenz und der Konstitution organische Verbindungen."
J. T. Hewitt—"Selective Absorption as Conditioned by Conjugate Linkage."
G. T. Morgan—"Colour and Constitution of Diazonium Salts."
G. T. Morgan and F. M. G. Micklethwait—"Para-diazo-imides and their Employment in the Production of Azo-dyes."
L. Mascarelli—"Sul contiguo di alcuni sostanzi organiche contenenti iodo plurivalente."

SECTION IV.a (2).—*Physiological Chemistry and Pharmacology.*

The following papers were communicated:—

- H. Meyer—"Relation between Lipoids and Pharmacological Action."
B. Moore—"Rôle of Lipoids and Unsaturated Acids in Hæmolysis."
M. Nicloux—"Mécanisme d'Action des Anesthetiques."
W. Straub—"Wirkungsmechanismus von Alkaloiden und Glykosiden."
G. Barger and H. H. Dale—"Constitution of Amines in relation to their Action on the Blood Pressure."

- O. Rosenheim—"Proposals for the Nomenclature of the Lipoids."
M. Aloy—"Sur les Precipitines."
N. A. Barbieri—(1) "Chemical Composition of Yolk of Egg: the Non-existence of Lecithin." (2) "Chemical Composition of Nervous Tissue."
H. Dreser—"Ueber alkalisch reagierende Medicamente."
P. Caccia—"Ricerche di determinazione della trimetil-ammina nella urine."
F. C. Cook—"Effects of Chloride, Sulphate, Nitrate, and Nitrite Radicles on the Frog's Heart."
P. Zanotti—"On Treatment of Infectious Diseases by means of some Bacterial Products."
A. Etard and A. Vila—"Sur les alkeminoides et les Chlorophylls."
G. Austerwell—"Sur l'influence de la pression sur les réactions d'isomerisation."

SECTION IV.b.—*Colouring Matters and their Application.*

The following papers were communicated:—

- P. Friedlander—"Ueber Kupenfarbstoffe." "Ueber Indigoidfarbstoffe."
M. Liebert—"Progress made in the Application of Synthetic Indigo and its Derivatives in the Textile and Dyeing Industries."
A. Wahl—"Sur quelques colorants indigoides, derives de la phenylisoxazolones."
H. Hollenweger-Marians—"Die Kupenfarbstoffe der Ges. f. Chem. Ind. in Basel."
T. Rosenberg—"Farbstoffe der Thioindigogruppe." The above five papers were discussed together.
M. Prud'homme—"Sur la formation du rouge d'paranitraniline."
E. Ehrmann—"Nouvelles matieres colorantes derivees de l'acide gallique."
A. Guyot—"Contributions a l'etude des phtaleines."
A. G. Green—"The Chemical Technology of Aniline Black."

SECTION V.—*Industry and Chemistry of Sugar.*

Meeting of the International Commission for the Unification of Methods of Sugar Analysis. The President of the Commission, Prof. HERZFELD, expressed his pleasure in holding this meeting of the Commission in London, and his thanks to the Sugar Section for offering the Commission the hospitality of their Section.

The official Agenda list of the Commission was as follows:—

- (1) Bericht über die Arbeiten der Kommission seit der letzten Sitzung in Bern am 3 und 4 August, 1906. Referenten: A. Herzfeld (Berlin), F. Strohmmer (Vienna).
- (2) Les tables de concordance entre la densité des solutions sucrées pures et leur teneur en sucre. Rapporteurs: E. Saillard (Paris), von Buchka (Berlin).
- (3) The clarification of the solutions of cane sugar for analysis. Referees: Prinsen Geerligs (Java), F. Sachs (Brussels).
- (4) Fortsetzung einer einheitlichen Nomenclatur für die Produkte der Zuckerfabrikation, besonders in Hinblick auf die Nahrungsmittel Gesetzgebung. Referent: F. Strohmmer (Vienna).

Prof. HERZFELD and Geh. Rat. STROHMMER gave short reports of the work of the Commission, and a discussion ensued.

Messrs. E. SAILLARD and BUCHKA gave their reports. As an outcome of the discussion on these reports it was resolved, on the motion of M. FRANÇOIS SACHS, "That a standard table at a temperature of 20° C. be officially adopted by the Commission, and that this table be based on the official German Table; and, further, that other tables at different temperatures (such as 15, 17½, 20, &c.) be calculated from the standard one, as also one according to the Mohr System at 20°/20°."

After discussion of the reports of Messrs. Prinsen Geerligs and Sachs, it was considered that, whilst the lead acetate

method might be used in the clarification of syrups was permissible, if excess were absolutely avoided, it was not advisable, at present, to make the general adoption of this method official.

M. Strohmer's report was discussed, but it was not considered advisable at present to pass any official resolution thereon.

Some papers were then read in connection with the Commission, namely:—

C. A. Browne (New York)—“Use of Temperature Corrections in the Polarisation of Raw Cane Sugars and other Products upon Quartz-wedge Saccharometers.”

Dr. WILEY read a paper from Mr. BRYAN on the same subject. Whilst it was agreed that the temperature corrections now employed in the United States were not correct for low-grade sugars, no definite resolution on the subject was advisable at present. Dr. Wiley stated that arrangements were being made in the official laboratories in America to take all polarisation readings of raw and refined sugars at 20° C.

Dr. WILEY also read a paper from Mr. BRYAN on the use of lead acetate in the clarification of sugars.

The following papers were communicated:—

M. Decluy (Paris)—“Contribution à la theorie des fours à chaux.” Second Part.

Leon Pellet (Lille)—“L'emploi d'injecteurs pour l'imbibition rationnelle de la bagasse.”

P. Kestner (Lille)—“Les procedes Kestner-Lagrange pour l'épuisement des bas-produits.”

Leon Pellet—“Les progres a realiser dans l'évaporation en sucrerie de cannes.”

Lewis Eynon (London)—“Influence of Clarification with Basic Lead Acetate on the Valuation of Sugar-products, and the relation between the amount of Lead added and that precipitated.”

L. Eynon and J. M. Lane (London)—“Influence of Time and Use on the Capacity of Graduated Vessels.”

R. J. Caldwell and R. Whymper (London)—“Determination of Rotatory Power.”

H. Pellet (Paris)—“Dosage de la matiere seche dans les produits de la sucrerie de betteraves, de la sucrerie de cannes et de raffinerie.”

E. Saillard (Paris)—“Apropos de l'analyse des melasses ou masecutes de betterave.”

H. Pellet—“Proposition relative à l'adoption d'une methode internationale d'analyse des melasses de betteraves et des melasses de cannes. Clarification: dosage de l'eau: dosage des cendres: polarisation avant et apres inversion: dosage des reducteurs.”

Vladimir Stanek (Prague)—“Ueber das Austrocknen der Rohzuckerproben und ein Verfahren zur Vermeidung derselben.”

J. B. Puvrey, de Groulart—“La procede rapide de traitement des basproduits de sucrerie de betteraves, de sucrerie de cannes et de raffinerie par le systeme Karlik-Czapikowski.”

W. D. Horne—“Dry Lead Defecation in Raw Sugar Analysis.”

SECTION VI.b.—Fermentation. (Joint meeting with Section VI.a).

Mr. A. R. LING gave a short résumé of our knowledge of starch.

Prof. Fernbach and J. Wolff—“Transformation catalytique de l'emploi d'amidon.”

Dr. Fouard—“Recherches sur l'amidon.”

Messrs. J. L. Baker and H. E. Hulton—“Behaviour of Wheat Flour towards Bakers' and Brewers' Yeasts.”

“Toxicity of Flours towards *Saccharomyces cerevisiae*.”

Prof. A. J. Brown—“Semi-permeable Properties of the Barleycorn.”

Dr. Holderer—“Diastases de l'orge et du malt.”

Mr. A. R. Ling—“Production of Diastase in Malting.”

“Production of Colour in Malt.”

Dr. Wyatt—“Recent Progress in the Study of Yeasts and Fermentation.”

Prof. Van Laer.—“Apropos de la catalase.”

Mr. Baker—“Purchase of Malt on Analysis.”

Prof. Lindner—“Die botanische und chemische Charakterisierung der Garungs-Mikroben und die Notwendigkeit der Errichtung einer biologischen Centrale.”

It was moved by the CHAIRMAN, seconded by Prof. BROWN, and resolved:—“That this meeting being in sympathy with the suggestion of Prof. Lindner to form a central bureau for fermentation organisms, hereby empowers him to write to the Council of the Institute of Brewing as to how it could be put on a working basis.”

Dr. Henneberg—“Neue Untersuchungen über Bakterien die für das Garungsgewerbe von Interesse sind.”

Dr. Orla Jensen—“The Main Lines of the Natural Bacteria System and the Bacteriological Nomenclature.”

L. Mathieu—“Recent Studies in Lactic Fermentation.”

“Sur l'extrait sec des vins.” “Les variations du non-alcool dans les eaux-de-vie naturelles.”

Pablo-Diez—“Manipulations licites sur les vins de liqueur.”

C. Gimel—“Rétablissement des vins à goût d'acide sulfureux.”

Dr. H. Mastbaum—“Sur l'analyse des alcools et eaux-de-vie.”

W. Mestrazat—“Consummatur d'acide malique et formation d'acide dans la fermentur alcoolique independance de ces deux phenomenes.”

SECTION VII.—Agricultural Chemistry.

The following papers were communicated:—

Prianichnikov—“Ueber den Einfluss von calcium carbonat und Ammoniumsulfat auf die Phosphorsaureaufnahme aus verschiedenen Quellen.”

Ryce—“Composition of the Deposits of Potash Salts.”

Precht—“Bestandtheile und Eigenschaften der für die Landwirtschaft werthvollsten Mineralien der Kalisalzen.”

Lyon and Bizzell—“Changes Produced in Soil by Subjecting them to Steam under Pressure.”

Pickering—“Changes occurring in Heated Soils.”

Perotti—“Sul ciclo biochimico dell' anidride fosforico nell terreno agrario.”

Scurti—“La chimica del vino.”

Kuriloff—“Eigenschaften der Russischen Schwarzerde.”

Ingle—“The Mineral Constituents of Food-stuffs.”

Fresenius—“Ueber Schwankungen am Fettgehalt der Kuhmilch.”

Bertrand—“La question des engrais catalytiques depuis le dernier Congrès de Chimie Appliquée.”

Marre—“Le Manganese comme engrais catalytique.”

Javillier—“Le zinc comme engrais catalytique.”

Agulhon—“Le bore comme engrais catalytique.”

Aulard—“Desiccation des produits agricoles.”

SECTION VIII.a.—Hygiene.

The following papers were communicated:—

M. Rolants (Lille)—“Les matieres organiques colloïdales des eaux d'égout.”

M. Begault—“Épuration Biologique des eaux d'égout.”

J. H. Johnston—“Physical and Biolytic Factors in the Purification of Sewage.”

W. J. Dibdin—“The Ærotic Method of Sewage Treatment.”

W. D. Scott Moncrieff—“High Nitrification in Sewage Effluents.”

F. W. Stoddart—“Nitrification and the Absorption Theory.”

T. Grossmann—“Disposal of Sewage Sludge by Distillation with Superheated Steam.”

S. Rideal and W. T. Burgess—“Standards for Sewage Effluents.”

G. Fowler and E. Arden—“Disposal and Purification of Trade Effluents.”

Prof. Klason—“Treatment of the Effluent from Sulphite Cellulose Factories.”

SECTION VIII.b.—*Pharmaceutical Chemistry.*

The following papers were communicated:—

- P. W. Squire and C. M. Caines—"Standardisation of Potent Drugs and International Agreement with regard to it."
P. MacEwan and G. P. Forrester—"Variations in the Activity of certain Toxic Drugs, with Suggestions for an International Enquiry."
P. M. Mardetzschlager—"Ueber die Wichtigkeit einer einheitlichen Untersuchungsmethode in chem. Beziehung aller Medikamente, Drogen u.s.w., aller Pharmacopœiaen der Erde zur Identitätsnachweisung durch eine Commission aller Staaten."
E. M. Houghton—"Proposed International Standards for the Physiological Action of Heart Tonics of the Digitalis Series."
G. Morselli—"Della necessita die introdurre nelle farmacoee ufficiali il concetto di titolazioni fisiologica per talune droghe e preparati medicinati."
D. L. Howard, B. Howard, and O. Chick—"Standards for Purity of Quinine Compounds in different Pharmacopœias."

The following resolution was carried unanimously:—"That this meeting of the Pharmaceutical Chemistry Section of the International Congress of Applied Chemistry having received and discussed communications by Messrs. Squire and Caines and MacEwan and Forrester, resolves that it is desirable that an international enquiry should be instituted with a view to securing:—(1) Greater uniformity in the commercial supplies of potent drugs and the means for determining the same; and (2) Approximation in the pharmacopœias of the world to common standards of activity."

- W. Hale—"Toxicity of Acetanilide Mixtures."
J. P. Remington—"Chemistry of the U.S. Pharmacopœia from 1820 to 1909."
A. B. Lyons—"Progress in Standardisation of Pharmacopœial Drugs."
S. P. Sadtler—"Organic Compounds of the United States Pharmacopœia."
A. Seidell—"The Solubilities of the Salicylates of the U.S. Pharmacopœia in Aqueous Ethyl Alcohol Solutions at 25°." "Methods for the Determination of Salicylates."
J. Ubeda y Correal—"Les comprimés médicamenteux."

SECTION VIII.c.—*Bromatology.*

On the systems for the Control of the Food Supply in—Belgium, Dr. Wauters; Germany, Dr. Kerp; Canada, Dr. McGill; Switzerland, Prof. Schaffer; Netherlands, Prof. Wysman and Dr. Van Rijn ("Butter Control").
M. Taffe—"Sur l'analyse des laits saisis."
Messrs. Russell and Arnaud—"The Fat Standard in Milk."
Dr. Borda—"Sur les catalases et les peroxydases dans le lait de vache."

The International Commission on the Unification of Analytical Methods have issued the following account of their proceedings:—"La Commission s'est réunie les vendredi 28, samedi 29, et lundi 31 mai à 9 h.m., sous la présidence de M. André. Elle a arrêté un règlement d'ordre intérieur; puis elle a examiné et approuvé un projet de rapport sur son organisation et ses travaux. Elle s'est ensuite occupée des rapports sur l'unification des méthodes d'analyse préparés par MM. André, von Buchka, Chapman, Cribb, Laval, Schoep, Mastbaum, Piutti, Vandavelde, Wauters, Wiley (Voir Seance du samedi 29 de la section de bromatologie). Enfin elle a procédé au recrutement de quelques membres nouveaux et à la constitution de son bureau. M. von Buchka a été élu président; MM. Armand Gautier, Thorpe, Piutti, Schaffer, Wauters, Wiley, Wysman, vice-présidents; M. Vandavelde, secrétaire général.

Papers on the composition of brandy and other spirits were communicated by Dr. Girard, M. Guillon, M. Mastbaum, M. Mestre, M. Ordonneau, M. Rocques.

Resolution carried:—"That brandy is a product of the distillation of wine, and the term is synonymous with eau de vie de vin."

SECTION IX.—*Photo-Chemistry—Photography.*

- Dr. Luppé-Cramer—"Ueber die latenten Bilder der Röntgenstrahlen und anderer Energiearten."
Prof. Wilder D. Bancroft—"Reversal of the Photographic Image."
M. S. de Prokoudine-Gorsky—"Différents effets des sensibilisateurs sur les plaques sensibles selon les propriétés des bromures d'argent de l'émulsion."
Maximilian Toch—"Photo-chemical Deterioration of Oil Paintings."
Dr. C. E. Kenneth Mees—"Report on the Present Condition of Sensitometry."
F. W. T. Krohn—"International Standard Method of Marking the Speed of Photographic Dry Plates and Definition of the Standard Conditions under which such Speed Tests are to be carried out."
Dr. C. Winther—"On the Eder-solution."

SECTION X.—*Electro-chemistry—Physical Chemistry.*

- F. G. Donnan and R. Findlay—"Electrolysis of Brine with the Findlay Cell."
R. Taussig—"Prozesse der Kochsalz-Elektrolyse."
L. H. Baekeland—"Three Years' Practice of the Townsend Cell."
E. A. Sperry—"Function of Refrigeration in the Liquefaction of Chlorine." "Chlorine Detinning in Practice."
A. Cappadoro—"Utilisation of Electrolytic Chlorine for the Simultaneous Production of Hydrochloric and Sulphuric Acids."
E. Leriche—"Contribution à l'Electrolyse des solutions salines avec anode de Zinc." "Procédé de Fabrication Electrolytique du blanc de Zinc."
Prof. Kistiakowsky—"Passivity of Metals."
Prof. Tschugaeff—"Ueber anormale Rotations-dispersion."
S. Cowper-Coles—"Experiments to Prove that Electrodeposited Copper has a Similar Crystalline Structure to Cast Copper."
C. Marie—"Influence de la viscosité du milieu sur les valeurs de la surtension cathodique." "Recherches sur la depolarisation."
B. Kuriloff—"Chemische Kette."
Report of Committee on Physical Chemical Notation.
J. H. Pollok—"New Thermo-chemical Notation."
C. Fery—"Recording Thermo-electric Calorimeter."
J. Danne—"Sur un Nouveau Produit Radioactif de la série l'uranium."
P. Zacharius—"Adsorption."
H. R. Ellis and F. E. Weston—"Thermic Reaction in Vacuo."
W. Biltz—"Zur Frage nach der Temperaturabhängigkeit der Valenz."
E. H. Riesenfeld—"Dissociation of Calcium Carbonate."

SECTION XI.—*Law, Political Economy, and Legislation affecting Chemical Industry.*

The following papers were communicated:—

- Dr. E. F. Ehrhardt—"Influence of Patent Law on Chemical Industry."
Dr. Schweitzer—"Necessity for International Patent and Trade Mark Legislation."

The following motion was proposed and carried:—"That international committees be appointed representative of all the nations party to the Congress to consider and draft proposals for joint international patent and trade mark legislation, with a view to international uniformity, such proposals to be laid before the Congress of 1912 for discussion and further action.

- M. Lojano—"Procédé de fabrication industrielle de jus naturel de raisin frais nonfermente Pasteurise."
Dr. Osterrieth—"Die Internationale Markeneintragung."

Dr. COSTERRIETH moved the following resolutions:—"It is desirable that all manufacturing countries, notably Germany, Great Britain, and the United States, adhere to the Madrid Convention concerning international trade mark registration, and that this arrangement should be raised at the next conference in the sense that—(a) Registration of a trade mark at the Berne Bureau should only have a formal effect; (b) that the deposit at the Berne Bureau be independent of registration in the country of origin."—Unanimously carried.

Dr. Julius Ephraim—"Ueber die Founvorschriften für Patent-an-meldungen der Chemischen Industrie."

Dr. Baskerville—"Legal Status of Industries giving rise to Noxious Gases."

The following motion was carried:—"That an International Commission be appointed to establish uniformity in the control of the escape of noxious gases."

W. D. Harkins (Minonla)—"The Smelter Smoke Problem in the United States."

TUESDAY, JUNE 1ST.

SECTION I.—Analytical Chemistry.

The following papers were communicated:—

- A. Chaston Chapman—"Jaffé's Colorimetric Method for the Estimation of Creatinine."
- Robert Adan—"Sur l'unification des méthodes d'analyse des essences résineuses."
- F. E. Weston and H. R. Ellis—"Estimation of Sodium Cyanamide and Nitrolim."
- G. D. Macdougald—"Improved Apparatus for Rapid Estimation of Specific Gravity."
- John Hughes—"The Question of Official Methods of Agricultural Analyses."

SECTION II.—Inorganic Chemistry and Allied Industries.

The following papers were communicated:—

- F. W. Clarke—"Chemical Work of the United States Geological Survey."
- J. Bruce-Kingsmill—"Sulphuric Acid—Recent Improvements in the Method of Intense Working."
- F. Raschig—"Bestimmung der schwefligen Säure in den Gasen der Blei-Kammer."
- L. Schucht—"Entwicklung der chemischen Tätigkeit auf dem Gebiete der Superphosphatfabrikation."
- M. G. Levi—"La reazione tra acido borico e coloruro sedico e la sua applicazione tecnica."
- H. Bassett—"Phase Relationships of the Calcium Phosphates and their Bearing upon certain Agricultural and Biological Problems."
- J. F. Bottomley—"Fused Silica Ware."
- N. Parravano and G. Tommasi—"T sali dell' acido Tiofenilacitico."
- W. Parravano—"T tungstati anidri."
- A. S. Cushman—"Contribution of Chemistry to the Art of Road Building."
- E. C. E. Lord—"Composition and Physical Properties of Slag for Road Building."
- P. Hubbard—"Examination of Bituminous Road Binders."
- P. Siedler—"Über Künstliche Zeolithe und deren Verwendung insbesondere zur Enthärtung, Entmanganung und Enteisung von Wasser."
- H. C. Demming—"Some Properties of Cadmium."
- L. Hackspill—"Sur les alliages du Platine avec les métaux alcalins et avec le Thallium."
- J. Perten—"Über neue Verfahren der Holzimprägnierung."
- L. Marino—"Per la conoscenza dei composti sopraossigenati."
- G. Pollacci—"Azione catalitica del carbonato di potassio sulla azotazione del carburo di calcio."

SECTION III.a.—Metallurgy and Mining.

- B. C. Kershaw (Liverpool)—"Fuel Purchase upon a Scientific Basis and the Control of Fuel Combustion."
- B. G. McLellan (York)—"Problems Involved in the Production of 'Power Gas' from Low-grade Fuels."
- M. Sepulchre (Paris)—"Gazogenes a fusion de centres."
- A. B. Searle (London)—"Gas Producers in connection with the Smelting of various Metals and the Utilisation of Poor Fuel."
- A. Victor Kochs (Sheffield)—"Koppers' Coke-oven and By-product Plant."
- E. Lloyd (Manchester)—"Simon-Carves' Coke-oven."
- D. Bagley (London)—"By-product Coke-oven in Great Britain."
- Olof Rohde (Stockholm)—"Chief Principles of Economic Firing and an Apparatus for this purpose."
- Umbert Savoia—"Remarques sur la fonte malleable."
- Dr. R. Adan—"Utilisation of Bronze and Nickel as Anti-friction Metals."
- Prof. D. E. Pannain (Via della Zecca, Rome)—"Le variazioni della struttura e della proprietà fisiche delle legne sottoposte alle azioni meccaniche e termiche."
- Dr. C. H. Desch (London)—"Eutectic Alloys."
- A. Gorboff (St. Petersburg)—"Über die Gesetzmässigkeit der Zusammensetzung der eutectischer Mischungen."
- M. Portevin—"Contribution a la discussion sur les eutectiques."
- Prof. Guillet—"Emploi de l'amortissement des mouvements vibratoires pour l'étude des fers et des aciers."

SECTION III.b.—Explosives.

- Capt. M. B. Lloyd—"Standardisation of Explosives as regards both the Diameter, Weight, and Strength of Blasting Cartridges."

Resolved:—"That the standardisation of blasting cartridges in respect of their diameters and weights is desirable, and that the details be referred to a sub-committee composed of members having knowledge of both mining and explosives."

- Dr. Robert Robertson—"Decomposition of Nitro-glycerin."
- G. W. Patterson—"Stability Tests of Smokeless Powders."
- C. G. Storm—"Potassium-iodide Starch Paper."
- Prof. A. R. Gaspar—"Etudes comparatives des divers tests de stabilité."
- Prof. W. Galloway—"Coal-dust."
- Richard Forstmann—"Coal-dust Question in Germany."

SECTION IV.a (1).—Organic Chemistry and Allied Industries.

- M. Padoa—"Fototropia dei fenilidrazoni."
- G. Ciamician—"Azioni chimiche della luce."
- M. Delepine—"Préparation de l'aldéhyde crotonique."
- R. Fabiny—"A New Method for the Exact Estimation of Nitrogen in Organic Substances."
- E. Bulmann—"Isomerism and Spacial Formulæ of the Cyanamic Acids."
- E. Mameli—"Sulla 4:5 dinitro-1:2-metilenpirocatechina."
- "A-Ossi-B-ossialchilderivati delle olefine aromatiche e catena propiliche." "Formazione di acetofenoni sostituiti dai del propilbenzolo."
- Anna Mammessier—"La tiocanferimide e la canfidina."
- B. Oddo—"Sull' idomagnesiopirrollo e il suo impiego per la sintesi dicomposti pirrolici." "Nuovo metodo di preparazione del nitrosobenzolo." "Su alcuni composti organici del mercurio."
- F. Konek-Norwall—"Beitrage zur Kenntniss organischer Bisulphide."
- P. Biginelli—"Artificial Tannin."
- F. C. Palazzo—"Sulla pseudomeria dell' isatina." "Sulla struttura degli acidi idrossammina."
- A. Piutti—"Derivati p-amminofenolici di acidi bicarbonici non saturi."
- Oliveri—"Sintesi col diazometano, Nuova preparazione del pirazolo."

- F. B. Power and H. Rogerson—"Chemical Examination of Jalap."
- A. Guyot (with M. Gry)—"Sur quelques nouvelles synthèses de vanilline."
- C. Bargellini—"Azione dell' acido solforico sulla santolina."
- H. A. D. Jowett and F. L. Pyman—"Relation between Chemical Constitution and Physiological Action, more particularly as exemplified by the Tropicines, the Aromatic Arsenic Acids, and the Alkamine Esters."
- G. T. Morgan and F. M. G. Micklethwait (with G. S. Whitby)—"Organic Derivatives of Arsenic and Antimony."
- G. T. Morgan and E. A. Cooper—"Germicidal Action of Arsenic and Antimony Compounds on Bacillus Typhosus."
- F. Garelli and G. De Paoli—"Processo di lavorazione industriale della materie grasse colmezzo dell ammoniaca."

SECTION IV.a (bis).—*Physiological Chemistry and Pharmacology.*

- L. Hugounenq et A. Morel—"Sur l'hydrolyse des matières albuminoïdes. Procédés nouveaux. Etude du phénomène." "Sur de nouveaux produits de l'hydrolyse des matières albuminoïdes."
- H. Stendel—"Ueber die Nucleinsäure."
- P. Thomas—"La présence et la recherche de l'émulsine intestinale."
- A. J. J. Vandeveldt—"Concerning Anti-enzymatic Reactions."
- R. A. Hasselbalch—"Action of Light on Blood and Blood-pigments, Sensitization."
- S. Mokrzecki—"Chemical Composition of Bile by a New Method."
- F. Mosca—"Le fermentazione della tirosina."

SECTION IV.b.—*Colouring Matters and their Application.*

- P. Lemoult—"Nouvelle série de leucobases et de matières colorantes."
- J. C. Cain and P. May—"Colouring Matter of Red Sanderswood."
- H. T. Bucher—"Azofarbstoffe."
- A. G. Green and A. E. Woodhead—"Action of Amines on Triphenylcarbinol and Tritolylcarbinol."
- R. Fosse—"Sur les sels de Pyryle."
- J. C. Cain—"Preparation of Monoacetyldiamines of the Benzidine Type." "Paranitrosomethyl-ethylaniline: a New Intermediate Product for the Manufacture of Dye-stuffs."
- E. de B. Barnett, T. P. Hilditch, and S. Smiles—"Derivatives of S-phenylphenazothionium."
- R. Vidal—"Sur le mécanisme de la coloration et de la teinture."
- A. Seyewetz and L. Poizat—"Sur l'oxidation des dérivés nitres et intrés par le persulfate d'antimonique."
- S. von Kapff—"Ueber ein neues Verfahren zum Durchfärben dichter Stoffe."
- J. Garçon—"La bibliographie des industries tinctoriales, leur repertoire analytique universel."

SECTION V.—*Industry and Chemistry of Sugar.*

- E. Saillard (Paris)—"Composition Minérale de la betterave."
- L. Rivière (Paris)—"Traitement des jus de diffusion et autres liquides sucrés par l'acide fluosilicique et les fluosilicates solubles." "Fabrication et emplois industriels de mélasse dépotassées." "Transformation des fluosilicates alcalins en carbonates."
- Henri Pellet (Paris)—"Sur la pureté réelle des petits jus de diffusion." "Sur la pureté réelle et la pureté apparente dans le contrôle de la sucrerie de cannes et de betteraves." "Influence de la concentration des produits purs et impurs sur la détermination de la densité."
- D. L. Davoll, jun. (Guantanamo).—"The Analysis of Bagasse."

Guiseppo Massobrio (Genoa)—"Utilizzazione dei residui della depurazione dei sughi (schiume dei defecazione) per la fabbricazione del cemento."

F. Zerban (Lima)—"Studies on Sulphitation in the Cane-sugar House."

L. K. Boseley (London)—"Sugar and Corn Syrup (Starch Glucose) as Raw Materials for the Confectionery and Preserves Industries."

K. Andrik, V. Bartos, and J. Urban (Prague)—"Ueber Variabilität des Gewichtes und des Zuckergehaltes der Zuckerrübenwurzel und über die gegenseitigen Beziehungen dieser beiden Merkmale."

J. Urban (Prague)—"Ueber die Bestimmung des Invertzuckers in der Rübe."

K. Andrik (Prague)—"Ueber die Darstellung des Adenins aus Melasse-abfalläugen." "Ueber Guaninpentosid aus den Melasseabfalläugen."

K. Andrik and J. Urban (Prague)—"Einfluss der Ernährung auf die Variabilität der chemischen Zusammensetzung der Rübe im Ersten Vegetationsjahre."

C. A. Browne and A. H. Bryan (Washington)—"Analysis of Commercial Dextrins."

L. T. Thorne and E. H. Jeffers (London)—"Some Points in the Technical Analysis of Mixtures of Sugars."

A. R. Ling (London)—"Analysis of Molasses for Distillery purposes."

Francesco V. Vidal (Mexico)—"Utilisation des vinasses épuisées en distillerie de mélasse de canne ou de jus de canne, en vue d'obtenir de l'azote sous forme de engrais."

SECTION VI.b.—*Fermentation.*

Prof. P. Petit—"L'azote assimilable des Moûts de Bière."

Prof. Windisch—"Ausblicke auf dem Gebiete der Malzerzi und Sudhaus-Arbeit."

Dr. C. Gasser—"On the Desirability of an International Definition of Beer."

Mr. Lott and Mr. Matthews—"Secondary Fermentation in English Beers."

Mr. Lott—"A Comparison of English and Lager Beers."

Dr. Schonfeld—"Die Eigenschaftsbeeinflussungen obergrüger Brauerei-Hefen."

Dr. Wyatt (in conjunction with Messrs. Schlichting and Winther)—"Do the Raw Cereal Products used in Brewing Contribute any Yeast Food to Beer Wort?"

Mr. Maynard—"Comparison of English and Continental Brewing Plant."

A. Chaston Chapman—"Rôle of Hops in Brewing."

Drs. E. Schlichting and H. Winther—"Criticism of Staining for Determining the Dead Cells of Yeast."

SECTION VII.—*Agricultural Chemistry.*

(Joint Session with Section VI.a).

Prof. Kosutany—"Zur Analyse des Mehles mit Rücksicht auf seine Backfähigkeit."

Messrs. Humphries and Simpson—"Gas-making capacity as a factor in the Estimation of Strength in Wheat and Flour."

Prof. Neumann—"Betrachtungen über die Backfähigkeit der Mehle."

Messrs. Le Clerc and Leavitt—"Influence of Environment on the Composition of Wheat."

Prof. Leather—"Effect of Manures on the Composition of the Grain of Field Crops."

MM. Mamell and Pollacci—"Ricerche sull' assimilazione diretta dell' azoto atmosferico nei vegetali."

Prof. von Feilitzen—"Employment of Artificial Cultures of Leguminous Bacteria for Soil Inoculation."

Mr. Hutchinson—"Use of Artificial Cultures for the Inoculation of Non-leguminous Plants."

Messrs. Hutchinson and Marr—"Changes Induced by the Addition of Carbohydrates to Soils."

Messrs. Voorhees and Lipman—"Investigations relative to the Use of Nitrogenous Manures."

M. Alluard—"Fabrication d'une farine sucrée propre à l'alimentation humaine et animale."

- MM. Grimbart and Bagros—"Sur le Mécanisme de la dénitrification chez les bacteries dénitrifiantes indirectes."
M. Laval—"L'autoéchauffement de la grosse Toile d'emballage."
Prof. Huston—"Field Experiments with Plant Foods."
MM. Pouget and Chouchak—"Sur l'absorption de l'acide phosphorique par les plantes."
M. Fabiny—"Ueber die Refraktion der Büffelmilch."
M. Vivien—"Le fumier de ferme."

SECTION VIII.a.—*Hygiene.*

- H. R. Kenwood and F. N. Kay-Menzies—"Chemical Evidence of Slight Sewage Contamination of Sea-water."
W. E. Adeney—"Determination of the Rate of Absorption of Atmospheric Oxygen by Polluted Waters."
J. E. Purvis, G. H. Macalister, and E. Minnett—"Action of Sea-water in the Decomposition of Sewage."
Aug. Aulard—"De la pollution des cours d'eau par les eaux résiduaires des sucreries, &c."
Dr. Somerville—"Phosphorus in Food-stuffs."
Drs. Goadby and Goodbody—"Lead Absorption and Lead Poisoning."

SECTION VIII.b.—*Pharmaceutical Chemistry.*

- E. Bourquelot—"Emploi de l'emulsiue a la recherche des glucosides dans les vegetaux." "Des glucosides cyanhydriques fournissant, dans leur doublement, de l'aldehyde benzoique ou de l'acetone."
G. Garbarini—"Purificazione dell' Etere sulfurico dai perossidi."
M. Patein—"Contribution a l'etude chimique des serums therapeutiques."
J. Effront—"Ueber den Nahrwerth der bei der Zersetzung der Proteinstoffe mit concentrirten Mineralsauren entstehenden Produkte."
L. Carcano—"Dove si fissa l'iodio nella molecola albuminoide vivente."
M. Watanabe—"Constituents of Henbane and Stramonium Cultivated in Japan." "Constituents of Herba Scopolia Japonica."
M. Hamburg—"Zur Untersuchung und Beurteilung von Malz-extracten."
H. Swan—"Suggested Improvement for Preparing Tincture of Ipecacuanha."

SECTION VIII.c.—*Bromatology.*

- F. W. Beck—"Advantages and Disadvantages of Legally Binding Standards for Foods and Drugs."
Dr. Albahary—"L'acide oxalique dans le Cacao et le Chocolat."
Dr. Borda—"Sur la composition des Cacaos."
Norman P. Booth—"Need for a Definition of Chocolate for Great Britain."
Dr. Girard—"Sur la présence et le dosage d'acide oxalique dans les Cacaos."
Pierre Dameland—"Présence de l'acide oxalique dans les Cacaos."
M. Menier—"Sur la composition des Chocolats."
Dr. Wauters—"Recherche de la graisse de Coco dans le Chocolat."

SECTION IX.—*Photo-chemistry and Photography.*

- A. J. Newton—"Report on the Present Condition of Etching Methods."
W. Gamble—"Acid Resists."
Dr. S. E. Sheppard—"Report on Colloid Chemistry in relation to Photography."
W. F. Cooper, W. H. Nuttall, and G. A. Freak—"Use of Agar-agar in Photography."
C. W. Gamble—"Note on Gelatose: Cause of certain Variations in the Sensitiveness to Light of Mixtures of Gelatose with Alkali Bichromate." "Action of Chromium Compounds on Gelatin, Historic Summary."

- H. M. Reichenbach—"Photographic Films of Nitro-cellulose."
Prof. R. Namias—"Sur un important perfectionnement apporté par M. Danesi aux méthodes et aux machines pour la photo-collography."
Prof. W. N. Hartley—"Aids to Photomicrography with Radiations of Short Wave-length."
A. and L. Lumiere and Seyewetz—"Sur le traitement simplifié des plaques autochromes et la correction des erreurs de temps de pose au cours du développement."
E. Howard Farmer—"Reproduction of Autochromes on Paper."

SECTION XI.—*Law, Political Economy, and Legislation affecting Chemical Industry.*

- M. Dupont-Rougier—"Rapport sur le dépôt et l'utilisation des plis cachetés."
Dr. Day—"Work done in the Commission on International Standardisation of Petroleum Oil."
Yu Tung Kwai—"Present Attitude and Future of Chemical Industry in China."

The following resolutions were passed and carried unanimously:—

"That an International Commission be appointed for the study of technical rules defining requisites, to which should correspond the principal chemical products, commercially known as 'commercial products.'"

(a) "That the work of this Commission should be considered as part of the work of the Congresses of Applied Chemistry."

(b) "That a Sub-section dealing with the Chemistry of Petroleum should in the future be a Sub-section in the Congresses."

"That the Congress expresses the wish that there should be created an international 'dépôt de plis cachetés.'"

REPORTS OF PRESIDENTS OF SECTIONS.

Report on SECTION I.: Analytical Chemistry.—This section held six full sessions, including four joint sessions. Out of a total of 105 papers presented to the section, 60 have been read and discussed. Some Reports have been received and several resolutions were adopted.

Report on SECTION II.: Inorganic Chemistry and Allied Industries.—This section has held seven sittings and one joint sitting with Sections III.b, IV.a, VII., and X., and 47 papers have been read.

Report on SECTION IV.a. 1: Organic Chemistry and Allied Industries.—Six sittings of this section have been held, including one joint meeting with Section XIV.b. The papers presented to this section amounted to 111, of which 60 have been read at the following meetings:—

First Sitting: Friday morning, May 28th—Five papers were communicated, and a discussion was initiated on "The Prospects of the Tar Industry, having in view the probable increase in the production of tar consequent on the adoption of the by-product coke oven."

Second Sitting: Saturday morning, May 29th—Eight papers were communicated.

Third Sitting: Monday morning, May 31st—Fifteen papers were communicated.

Fourth Sitting: Monday afternoon, May 31st—Joint meeting with Section IV.b. Eight papers were communicated, one of these being from Section IV.b.

Fifth Sitting: Tuesday morning, June 1st—Eighteen papers were communicated.

Sixth Sitting: Tuesday afternoon, June 1st—Seven papers were communicated.

Report on SECTION IV.b: Colouring Matters and their Application.—The section has met on five occasions, and has also held a joint meeting with Section IV.a. The number of communications read (or taken as read) before the section was 52.

Report on SECTION IV.a bis: Physiological Chemistry and Pharmacology.—Five meetings were held, including the joint meeting with Section VI.b. Sixty-six papers (including the demonstrations) were presented. Of these 46 were read.

Report on SECTION V.: Industry and Chemistry of Sugar.—The section held seven sittings. Sixty-eight papers were read before the section, and animated discussions followed most of these papers. Several Committees were appointed to investigate points of special interest and to further unification of methods of general and technical sugar analysis.

Report on SECTION VI.b: Fermentation.—Seven sittings of the section have been held, of these two were joint meetings. Fifty-eight papers have been read and discussed out of 94 printed. A joint meeting with Section IV.a bis was held on Saturday, May 29th. At this meeting demonstrations were given and physiological papers were read. Another joint meeting with Section VI.a was held on Monday, May 31st, at which papers dealing with Starch and Malting were read.

Report on SECTION VII.: Agricultural Chemistry.—Friday, May 28th: Morning Meeting—Four papers were read; Afternoon Meeting—Three papers were read.

Saturday, May 29th—Five papers were read.

Sunday, May 31st: Morning—Seven papers were read; Afternoon—Eight papers were read.

Tuesday, June 1st: Morning—Five papers were read; Afternoon—Eleven papers were read.

Report on SECTION VIII.a: Hygiene.—The section of Hygiene has held six sessional meetings and two joint sessional meetings during the Congress. Thirty-six papers were presented, and of these 28 were read and discussed. The papers dealing with such subjects as the sterilisation of water by ozone, lead poisoning, the purification of sewage by various methods, and the contamination of sea water by sewage, gave rise to a considerable amount of interesting discussion.

Report on SECTION VIII.b: Pharmaceutical Chemistry.—This section has held five sittings, and also one joint sitting with Section VIII.a. Forty-four communications were submitted (in addition to five at the joint sitting), and of these forty were read and discussed.

Report on SECTION VIII.c: Bromatology.—The Section held in all seven meetings, of which three were joint meetings with Section I. (Analytical Chemistry), in one of which Section XI. (Law, Political Economy, and Legislation affecting Chemical Industry) also joined, and one was on the occasion of a joint discussion with members of the Hygiene Section VIII.a. The meetings were mainly devoted to the discussion of the subjects comprised in the following list, on each of which subjects a number of communications were presented:—

1. "Systems for the Control of the Food Supply."
2. "The Composition and Analysis of Brandy."
3. "The Advantages and Disadvantages of Legally Binding Standards of Composition for Foods and Drugs."
4. "Chocolate, its Composition and Analysis."
5. "The Use of Preservatives in Foods."

In addition to the above meetings, one morning (May 31st) was devoted to the reception of reports from the International Commission for the Unification of Analytical Methods, which body held short sessions on the mornings of May 29th and 31st, and June 1st, between 9 and 10 a.m. On the occasion of the discussion on brandy a resolution was passed embodying a definition of the word "brandy." In all, 42 papers were read out of 85 received or promised.

Report on SECTION IX.: Photochemistry—Photography.—This section has held five sittings and received and discussed 27 papers. Prof. R. Namias, in the name of the Societa Fotografica Italiana, of Florence, has laid before the section a proof copy of an album of photographs of Messina and Reggio illustrating the results of the recent

earthquake. A complete copy will shortly be presented to the Congress.

The following resolutions from the Sections have been passed:—

Section I.

i. "En vue d'unifier les méthodes d'analyse et de recherche dans l'essai des essences de produits résineux, le congrès international de chimie appliquée émet le vœu de voir s'établir par les soins de la Section I. un tableau définissant les bases à utiliser dans l'estimation la pureté des soudits produits et dont l'usage serait fortement recommandé à tous les analystes."

ii. "The Institution of Official Methods for Agricultural Analyses is undesirable, unless subject to periodical revision."

iii. "The seventh International Congress of Applied Chemistry considers that it is desirable to adopt uniform principles in connection with the application of reference tests, and is of opinion that the proposals made by Prof. T. W. Fresenius constitute a suitable basis for these principles."

Section IV.a bis.

"That the section in future Congresses be a separate and independent section entitled Biochemistry, including Pharmacology."

Section VI.b.

"That this meeting, being in sympathy with the suggestion of Prof. Lindner to form a central bureau for fermentation organisms, hereby empowers him to write to the Council of the Institute of Brewing (London) as to how such a project could be carried into effect."

Section VIII.a.

i. "That the Congress requests the various governments to nominate a Commission to make researches, in collaboration with manufacturers, on materials used in the ceramic arts, to encourage the use of substances not containing lead; to restrain the use of lead materials, and to conduct further researches with regard to protective materials for the hygienic use of those engaged in the ceramic industries."

ii. In conjunction with Sections III.a. and XI.:—

"The Congress is requested to appoint a Committee to impress upon the Governments of each country represented at the Congress the importance of adopting a uniform law throughout their respective territories regarding the emission of noxious fumes from chemical and metallurgical works, and of black smoke from works and factories. The Section believes that the abatement of atmospheric pollution will be most rapidly secured by placing the control of all such gaseous emanations in the hands of fully qualified inspectors capable of giving the necessary technical advice to manufacturers. It records its conviction that the dispersal of the pall of smoke covering certain industrial districts in England and elsewhere will be accompanied by enormous benefit to the inhabitants, and will prove an ultimate gain to the manufacturer."

iii. "L'épurations des eaux obligation, attendu que les moyens pratiques et chimiques pour la réaliser, ne mangent pas et que l'industriel en retirera bénéfice."

Section VIII.b.

"That this meeting of the Pharmaceutical Chemistry Section of the International Congress of Applied Chemistry having received and discussed communications by Messrs. Squire and Caines and MacEwan and Forrester, resolves that it is desirable that an international enquiry should be instituted with a view to securing:—(1) Greater uniformity in the commercial supplies of potent drugs and the means for determining the same; and (2) Approximation in the pharmacopœias of the world to common standards of activity."

"With a view to advancing these objects this meeting further recommends that the following Provisional Com-

mittee be appointed to inquire and report on the subject to the next meeting of the Congress:

Messrs. P. W. Squire and F. Ransom (Great Britain).

Prof. H. Thoms and E. Schmidt (Germany).

Prof. E. Bourquelot and M. Leger (France).

Profs. Piutti and Guareschi (Italy).

Profs. Remington and Rusby (United States), with P. MacEwan (Great Britain and U.S.A.), and G. P.

Forrester (European Continent) as Secretaries.

"This meeting recommends that the Provisional Committee shall have power to invite as members with equal rights persons who have interested themselves in this subject, and further that this resolution shall be conveyed to the Governments and pharmacopœial authorities who were represented at the Brussels Conference (1902) on the unification of potent remedies."

Section XI.

i. "That the Committee of the various countries party to the International Convention for the Protection of Industrial Property be requested to consider the desirability of adopting the following provision: 'The manufacture in one country of the Union protects the patentee against the revocation of his patents in all countries of the Union.'"

ii. "The Section recommends the question raised by M. de Laire's paper on 'The International Patent' to the attention of the International Association for the Protection of Industrial Property and to the National Committees for study with a view to future Congresses."

iii. "That International Committees be appointed representative of all the nations party to the Congress to consider and draft proposals for joint international patent and trade mark legislation, with a view to international uniformity, such proposals to be laid before the Congress of 1912 for discussion and further action."

iv. "That the Congress deprecates any patent legislation limiting the patentability of pharmaceutical products."

v. To commit the question of international acknowledgment of the right of prior use within the States adhering to the International Convention to the International Association for the Protection of Industrial Property for further consideration."

vi. "That the Congress expresses the wish that there should be created an 'international dépôt de plis cachetés.'"

vii. "That it is necessary that a fancy name designating a medicinal compound of definite composition should be protected as a trade mark as securely as such a name applied to a secret remedy, or a remedy of indefinite composition."

viii. "It is desirable that all manufacturing countries, notably Germany, Great Britain, and the United States, adhere to the Madrid Convention concerning international trade mark registration, and that this arrangement should be raised at the next Conference in the sense that: (a) Registration of a trade mark at the Berne Bureau should only have a formal effect; (b) that the deposit at the Berne Bureau be independent of registration in the country of origin."

ix. "That an International Commission be appointed for the study of technical rules defining requisites, to which should correspond the principal chemical products commercially known as commercial products."

x. "That the work of this Commission should be considered as part of the work of the Congress of Applied Chemistry."

xi. "That a Sub-section dealing with the chemistry of petroleum should, in the future, be a Sub-section of the Congress."

xii. "That an International Commission be appointed to establish uniformity in the control of the escape of noxious gases."

xiii. "That each succeeding Congress of Applied Chemistry do examine and report upon the progress and

position of chemical industry in each of the countries party to the Congress, having particular regard to the country in which the Congress is for the time being held, and to the relation between the development of chemical industry and customs' tariffs."

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, May 14th, 1909.

Dr. C. CHREE, F.R.S., President, in the Chair.

A PAPER ON "A Bifilar Vibration Galvanometer" was read by Mr. W. DUDELL.

The paper describes a new type of vibration galvanometer and a series of tests made upon it. Vibration galvanometers may be divided into two types: (1) those in which the moving part consists of a piece of iron or steel and the current to be measured flows round fixed coils as in the case of the Thomson galvanometer; (2) those in which the current to be measured flows round a moving coil placed in a fixed magnetic field on the syphon recorder principle. The vibration galvanometers of Max Wien and Rubens belong to the first class, while Mr. Campbell's vibration galvanometer and the one described in the paper belong to the second. In the instrument described the mass of the moving parts is reduced to a minimum, the moving coil being reduced to the two wires forming its two sides, similar to a bifilar oscillograph, but with this difference:—Whereas the bifilar oscillograph is designed so as to make the damping aperiodic, the vibration galvanometer is designed so as to keep the damping as small as possible. A series of tests made upon the instrument showed that the total range of frequency was very large, namely, from about 90 vibrations per second up to 1900 vibrations per second. The damping is very small, so that the resonance is very sharp. A series of measurements on the sensibility of the instrument showed that the sensibility to alternating current decreases very nearly inversely as the frequency for which the instrument is adjusted, whereas for direct current the sensibility decreases approximately inversely as the square of the frequency for which the instrument is adjusted, which is what usually takes place with direct current galvanometers. The sensibility of the galvanometer for detecting small alternating voltages is reduced by the back E.M.F. of the instrument, and the paper concludes with a determination of the magnitude of the back E.M.F. in the instrument shown at the meeting. The advantages of the galvanometer are its simplicity, ease in tuning, wide range of frequency for which it can be tuned, high sensibility, negligible self-induction, and comparatively small back E.M.F.

Mr. A. CAMPBELL said that thanks were due to the author for an interesting account of the valuable and thorough investigation he had made of the behaviour of single-loop bifilar vibration galvanometers. Galvanometers of this type had been used at the Reichsanstalt for several years (*Zeit. für Instrumentenkunde*, May, 1906) and had given good results with frequencies as high as 2500 vibrations per second. He did not know what sensitivity was obtained with the German instruments, but there was no doubt Mr. Duddell's pattern of the same type was much more sensitive than the instrument of the moving coil type which he (Mr. Campbell) described in 1907. Blondel pointed out in 1900 that in an oscillograph there was no advantage in having more than one turn of wire, but this appeared to be only true when the mirror was very small. As a large mirror with plenty of light and good definition greatly improved the ease and accuracy of observation, he gave the preference to a moving coil of more than one turn, even though the single-loop instrument was highly recommended by Dr. Orlich. With a

moderately large mirror one could obtain good definition of a dark line with a scale distance of 600 cm. Mr. Campbell mentioned that Wien's vibration galvanometer (*Ann. der Phys.*, 1901) with very small magnets and minute mirror gave 70 mm. at 1 metre distance for 1 microampere at 100 vibrations per second and had a resistance of 200 ohms. Mr. Duddell's curves were most instructive. He had verified experimentally the law which he (Mr. Campbell) had stated from theoretical considerations, namely, that with a given bifilar suspension (tuned to resonance) the sensitivity varies inversely as the frequency. The figures given tended to show that the shorter bifilars gave reduced sensitivity. With much shorter bifilars he had found great loss of sensitivity. In the moving coil type with many turns the back E.M.F. was considerable and might even double the effective impedance of the instrument and lower the volt-sensitivity accordingly.

Dr. J. A. FLEMING asked the author if he had tried his instrument with intermittent currents of the right frequency. If the galvanometer was sensitive to currents such as are obtained by rectifying trains of oscillations from condensers, it might be useful as an optical call in wireless telegraphic stations.

Dr. RUSSELL congratulated the author on the notable advance he had made in the design of vibration galvanometers. He much appreciated the clear presentation and the accuracy of the experimental results. He asked whether variations of the barometric pressure had any appreciable effect on the sensitivity of the instrument, and suggested that variations in the humidity of the atmosphere might possibly have some effect. So far as he was aware, the author was the first to point out the importance of the back electromotive force due to the vibrating wires cutting the magnetic field. He thought that the experimental results given would be a great help in formulating a more exact mathematical theory of this type of apparatus. He showed that to a first approximation the author's results were in agreement with those deduced from the differential equation ordinarily given for the motion of the mirror. He asked whether the frequency of ordinary alternating-current supply circuits was sufficiently steady to avoid the necessity of constant tuning of the apparatus.

The CHAIRMAN asked the author if the mirror was always situated in the middle of the vibrating fibres.

The AUTHOR, referring to Mr. Campbell's remarks, said considerations of space prevented him from working with scale distances of 6 metres. With regard to Wien's instrument it was easy to obtain high current sensitivity but not high voltage sensibility. He had tried Prof. Fleming's suggestion, but his instrument was not sensitive enough for ordinary signals. With more uniform spark frequency it gave excellent results. In reply to Dr. Russell, he stated that the sensitivity of the galvanometer did vary slightly with the barometric pressure. In the ordinary differential equation the term giving the moment of the applied forces needed amending, and so also did the term for the damping couple. The complete equation was complex and there were difficulties in the way of getting an exact solution. The frequency of ordinary supply circuits was quite constant enough for accurate work. In reply to Dr. Chree, he stated that the mirror was always symmetrically situated on the suspension.

A paper by Messrs. W. P. FULLER and H. GRACE on the "Effect of Temperature on the Hysteresis Loss in Iron in a Rotating Field" was read by Prof. MARCHANT.

The rotating field was produced by means of two phase currents. One phase was connected to a coil of long rectangular section and of sufficient length to produce a uniform field within a radius of 2 cm. from the centre. The second phase was connected to a similar coil enclosing this one and causing a flux at right angles to it. The resultant field at the centre was uniformly rotating. An iron disc 4 cm. diam., 0.027 cm. thick, was supported by a bifilar suspension and the torque measured by a mirror and

scale in the usual way. The specimen was heated by means of nickel wire heaters placed above and below it, and the temperature measured by means of a thermojunction placed close to the disc. The flux in the iron was measured by the voltage induced in a coil of eight turns of bare wire wound round it. To measure the voltage, the maximum value of which was of the order of 0.03 R.M.S. volts, a special galvanometer was constructed. This depends for its action on the forces exerted by a rotating field on a suspended coil carrying alternating currents. If E be the E.M.F. applied to the moving coil, and E_1 the E.M.F. due to the field on the coil, then, by turning the coils producing the field round until the deflection is a minimum, this deflection is proportional to $E - E_1$. The results of the experiments show that the effect of increasing the temperature of iron is to reduce the hysteresis loss at a given induction and to cause the maximum loss to occur at a lower value of the induction. In one specimen the maximum value of the loss at 220° C. was 12,300 ergs per cu. cm. per cycle at an induction of 16,000 C.G.S. units. At 580° C. the maximum loss was 2600 ergs at an induction of 10,700. The frequency of the experiments was 42 cycles per sec.

Dr. W. H. ECCLES remarked that the effects of previous thermal treatment, and of the nature of the material on the properties studied by the authors, were so enormous that comparison of the present experiments with similar ones with alternating fields was difficult; but the authors' curves seemed to show that the effect of rise of temperature on hysteresis loss was less for rotating fields than for alternating fields if the fields were below about 12 C.G.S. The curves showed also that the maximum values of hysteresis loss in rotating fields were reached at lower and lower flux densities the higher the temperature, although the permeability varied but little. This was of importance from the point of view of the molecular theory of magnetism; it showed that smaller forces sufficed to rotate the molecules within a magnetically stable group at high than at low temperatures. The authors' experiments might be regarded as adding strong confirmation to the molecular theory of magnetism.

Prof. MARCHANT said the iron tested was obtained direct from the manufacturers and its previous thermal treatment was not known. A permeability curve had, however, been obtained. He expressed his interest in Dr. Eccles's remarks upon the bearing of the experiments on the molecular theory of magnetism.

A paper "On a Method of Testing Photographic Shutters," by Messrs. A. CAMPBELL and T. SMITH, was read by Mr. SMITH.

The authors described a simple and rapid method of testing the speeds and efficiencies of photographic shutters, with a maximum error of 0.0001 second at the highest speeds. A vibrating beam of light falling through a narrow slit on to a moving plate serves to measure the time. This beam is obtained by reflecting the light of a Nernst lamp from the mirror (area 50 sq. mm.) of a vibration galvanometer actuated by a current of fixed frequency (say 100 or 500 vibrations per second) obtained from a microphone hummer. The use of the vibration galvanometer, in which the amplitude is enormously increased by resonance, greatly facilitates the measurements.

When the total duration of exposure only is required, the vibrating beam of light is passed through the shutter, tracing a sine curve on the moving plate. The duration of exposure is immediately found by counting the number of ripples recorded on the plate. Ten records of the various speeds of a shutter can be taken side by side on one 5" × 4" plate in one minute.

When the efficiency in addition to the duration of exposure is required, the method adopted is essentially that of Sir Wm. Abney, but the time measurements are made with the vibrating beam of light instead of a screen. The sine-curve now extends over the length of the plate and serves as a continuous time record, and is to be preferred

to any intermittent method of measuring the time. A slit is placed in a diameter of the shutter-opening as close to the shutter leaves as possible, and an image of a line source of light is made to fill this slit. By means of a concave mirror an image of this slit is formed on the plate by the side of the vibrating beam of light. As the shutter opens the length of the slit through which light can reach the plate increases, and the record on the plate gives the length of the slit which is opened at every instant of time. Measurements are then taken of the area of the shutter aperture corresponding to a number of lengths of the slit-opening. Combining these records the area of the shutter aperture at every instant of the exposure is obtained, and by integrating this area with respect to time the equivalent exposure at full aperture and the efficiency are calculated.

Mr. BAKER expressed his interest in the method, which he said was the most satisfactory yet produced. It was difficult to say exactly what to call exposure. In photographing moving objects it was advisable to use as the effective time the time during which the central eight-tenths of the shutter was open.

Mr. DUDDELL said the method was an ingenious one for determining the efficiencies of shutters. He suggested that by using an arc it might be possible to reduce the size of the mirror and thus work at higher frequencies. Instead of using a slit it might be better to use a short focus cylindrical lens.

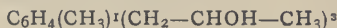
Mr. CAMPBELL, referring to Mr. Duddell's remarks, said that with a Nernst lamp it was possible to obtain high frequency curves showing very little tendency to tail off.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

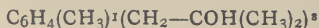
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlviii., No. 17, April 26, 1909.

Cuprous Sulphate.—A. Recoura.—By double decomposition between cuprous oxide and neutral methyl sulphate, cuprous sulphate is formed, $\text{Cu}_2\text{O} + \text{SO}_4(\text{CH}_3)_2 = \text{Cu}_2\text{SO}_4 + (\text{CH}_3)_2\text{O}$. When all the oxide has been converted into sulphate, the excess of methyl sulphate may transform the cuprous into cupric salt, but this reaction only occurs when the first is completed, and it is easy to guard against it. Cuprous sulphate is a greyish white powder, which is absolutely unaltered in dry air. Water decomposes it into cupric sulphate and copper with disengagement of 21 cals., and this explains the difficulty of isolating the salt.

Researches on Magnesium Derivatives of Bromides of Xylyls.—P. Carré.—The action of magnesium on ethereal solutions of bromides of xylyls gives chiefly ditolyethanes. The proportion of magnesium compound formed is much less than in the case of benzyl chloride. The bromide of metaxylyl, however, gives an appreciable amount of magnesium compound, the condensation of which with formaldehyde yields metatolyethyl alcohol, $\text{C}_6\text{H}_4(\text{CH}_3)(\text{CH}_2-\text{CH}_2\text{OH})^2$. With acetic aldehyde and acetone the alcohols formed are—



and—



respectively.

Oxidation of Aromatic Nitro- and Nitroso-compounds by Ammonium Persulphate.—A. Seyewetz and L. Poizat.—Ammonium persulphate in neutral, acid, or alkaline aqueous solution decomposes many nitro- and nitroso-compounds at 100°, giving hydrocyanic acid. Since ammonium persulphate does not decompose the HCN formed it could be used for the quantitative study of the reaction. The authors have shown that derivatives in which the ortho- and para-positions are occupied by

phenol hydroxyls, and in the molecule of which there are several nitro-groups, give considerable quantities of hydrocyanic acid when their aqueous solutions are boiled with ammonium persulphate. This phenomenon may be explained by supposing that the nitro-compounds yield iso-nitro derivatives, that the oxygen atom migrates from the nitrogen to the neighbouring carbon, giving a quinone, which is then oxidised with the formation of HCN.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 7th inst., Sir James Crichton-Browne, Treasurer and Vice-President in the Chair. Mr. A. E. Price and Dr. G. W. Steeves were elected members.

Faraday Society.—On Tuesday next, June 15, at 8 p.m., in the Library of the Institution of Electrical Engineers, Mr. E. R. Taylor, Chairman of the Conservation Committee of the American Electrochemical Society, will deliver an Address, illustrated with lantern slides, on "The National and International Conservation of Water or Power."

Seventh International Congress of Applied Chemistry.—We have received from the Dover Street Studios a set of fourteen proofs of groups of the various Sections, taken on the steps of the Royal College of Science on the morning of the last day of the Congress. The portraits are more than usually successful. Each separate group does not contain too many individuals, and the heads therefore are sufficiently large to make them valuable as separate likenesses, as well as interesting as forming parts of a group of workers in the same domain of applied science. We understand the complete set is to be published in the form of an album.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Estimation of Manganese.—What is the function of the silver nitrate in the Walters process for colorimetric determination of manganese (CHEMICAL NEWS, lxxiv., 239)?—J. WILLIAMS.

MEETINGS FOR THE WEEK

TUESDAY, 15th.—Faraday Society, 8. "The National and International Conservation of Water for Power," by E. R. Taylor. "Formation of Silicon Sulphide in the Desulphurisation of Iron," by W. Fielding. "Study of Electric Furnaces as applied to the Manufacture of Iron and Steel," by C. A. Keller. "Automatically Circulating Furnaces of the Gin Type for the Electrical Production of Steel," by G. Gin.

WEDNESDAY, 16th.—Microscopical, 8. Exhibition of the better-known Tropical Parasites, by Dr. J. A. Braxton Hicks.

THURSDAY, 17th.—Chemical, 8.30. "Carbonate of Copper and the Cupricarbonates," by S. P. U. Pickering. "Isoquinoline Derivatives—Part I., Oxidation of Laudanosine," by F. L. Pymau. "Colour and Constitution of Azo-compounds," by J. T. Hewitt and W. Thomas. "Isoimiazolone," by H. J. H. Fenton and W. A. R. Wilks. "Homologues of Furfural," by H. J. H. Fenton and F. Robinson. "Studies of Dynamic Isomerism—Part IX., Relationship between Absorption Spectra and Isomeric Change—Absorption Spectra of Sulphonic Derivatives of Camphor," by T. M. Lowry and C. H. Desch. "Relation between the Strength of Acids and Bases and the Quantitative Distribution of Affinity in the Molecule," by B. Flürscheim. "Oxidation of Hydroxy-derivatives of Benzaldehyde and Acetophenone," by H. D. Dakin. "Intramolecular Rearrangement of Diphenylamine-ortho-sulphoxides," by E. de B. Barnett and S. Smiles.

FRIDAY, 18th.—Royal Institution, 9. "A Recent Visit to the Panama Canal," by A. H. Savage Landor.

THE CHEMICAL NEWS.

VOL XCIX., No. 2386.

THE DECOMPOSITION OF NITROGLYCERIN.*

By ROBERT ROBERTSON, M.A., D.Sc., F.I.C.

THIS paper deals with the decomposition of nitroglycerin when free from the catalytic accelerative action produced by its volatile products of decomposition.

The difficulties due to the volatility of nitroglycerin and the risk of explosion are overcome by the use of the apparatus figured below.

Experimental Method.

Jena glass-wool soaked in 0.3 to 5 grms. nitroglycerin dissolved in acetone, which is subsequently evaporated off, is placed in the horse-shoe shaped tube, closed by a greased and mercury-sealed plug. A current of CO₂ can be sent down the right-hand spiral, through the glass-wool and up the other spiral, or *vice versa*, according to the

mined by the spectroscopic method of Robertson and Napper (*Journ. Chem. Soc.*, 1907, xci., 761), and from this the weight of nitrogen disengaged in the form of NO₂ was calculated. In most cases the gases issuing from the observation tube were then passed through hot reduced copper asbestos and copper oxide asbestos, and into a gas burette containing caustic potash solution, where the unabsorbed nitrogen is measured every quarter of an hour. The weight of nitrogen is calculated after deduction of the amount contained in the CO₂, the rate of which was uniformly 1000 cc. per hour.

Results and Conclusions.

The decomposition of nitroglycerin with continuous removal of volatile products was studied between the temperatures of 90° C. and 135° C., and the following results and conclusions obtained.

1. In the apparatus just described the decomposition of nitroglycerin proceeds in a manner as uniform as that of a stable guncotton when the volatile products of decomposition are continuously removed. Thus from 0.5 gm. nitroglycerin at 125° C., nitric peroxide is found by the spectroscopic method to be present in the stream of CO₂ in the following concentrations for sixteen successive quarter hours:—0.04, 0.07, 0.09, 0.11, 0.11, 0.12, 0.12, 0.12, 0.13, 0.13, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12.

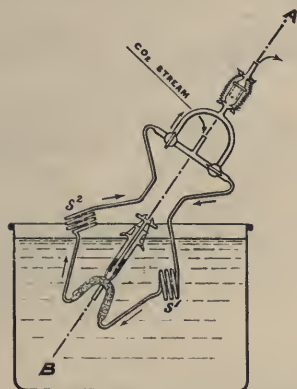


FIG. 1.—Decomposition Vessel, Rotating on Axis A B.

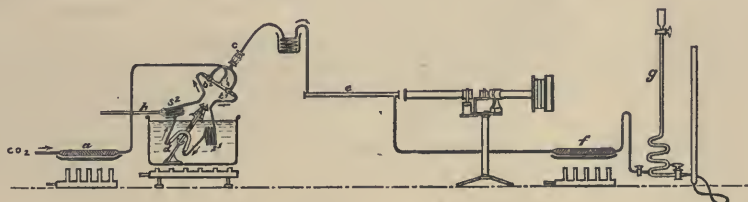


FIG. 2.—Apparatus for Estimating NO₂ and Total N from Nitroglycerin.

position of the stopcocks. At the upper end of the apparatus is a slip joint between which and a supporting pivot at the bottom the whole apparatus can be rotated about its axis. The CO₂ used contained only 0.02 per cent of gas unabsorbed by KOH solution, and, to eliminate any oxygen, was passed over red-hot copper asbestos. Spiral s¹ is immersed in an oil-bath, the temperature of which is known, and is maintained uniform by a stirrer. It serves as a preheating worm for the CO₂. Spiral s² is above the heated oil, is protected from it by asbestos cards and is cooled by an air-blast. It serves to condense any volatilised nitroglycerin. After a suitable period the apparatus is rotated through 180 degrees, when the spirals exchange functions. Any nitroglycerin which had condensed in s¹ is now restored to the system. The gaseous products of combustion are led off for examination through the slip joint by means of fixed glass tubes, the use of indiarubber being thus avoided. As a precaution against the carrying over of nitroglycerin the gases pass through an ice-cooled worm immediately on leaving the decomposition apparatus. The mixture of CO₂, of which the volume is known and rate uniform, and volatile products of decomposition was usually passed through an observation tube, in which the concentration of NO₂ was deter-

2. The nitrogen is disengaged from the nitroglycerin as nitric peroxide, since the estimation of nitrogen existing as nitric peroxide agrees with the results of estimation of total nitrogen by combustion, and of other methods. In this respect nitroglycerin differs from guncotton, from which the nitrogen is disengaged (at 135° C.) as nitric peroxide to the extent of about 40 per cent of the total. This is evident from the accompanying table, which includes also the disengagement of total nitrogen from guncotton according to Will.

Mgms. Nitrogen from 2.5 grms. per Quarter Hour.

Temp., °C.	Nitroglycerin.		Guncotton.	
	Total N by combustion.	N as NO ₂ by spectroscopic observation.	Total N (Will, 2. Mitt. Zentralst.).	N as NO ₂ (R. and N., J. C.S., xci. 775).
135.0	4.87	4.33	0.55	0.23
130.0	2.72	2.90	0.26	—
124.9	1.62	1.57	0.12	—
119.8	0.74	0.80	—	—
115.0	0.36	0.39	—	—
110.2	0.20	0.20	—	—
105.0	0.10	0.086	—	—
100.5	0.044	0.043	—	—
95.0	0.021	0.024	—	—
90.3	0.009	0.010	—	—

* Abstract of Paper read at the Seventh International Congress of Applied Chemistry, London, 1909.

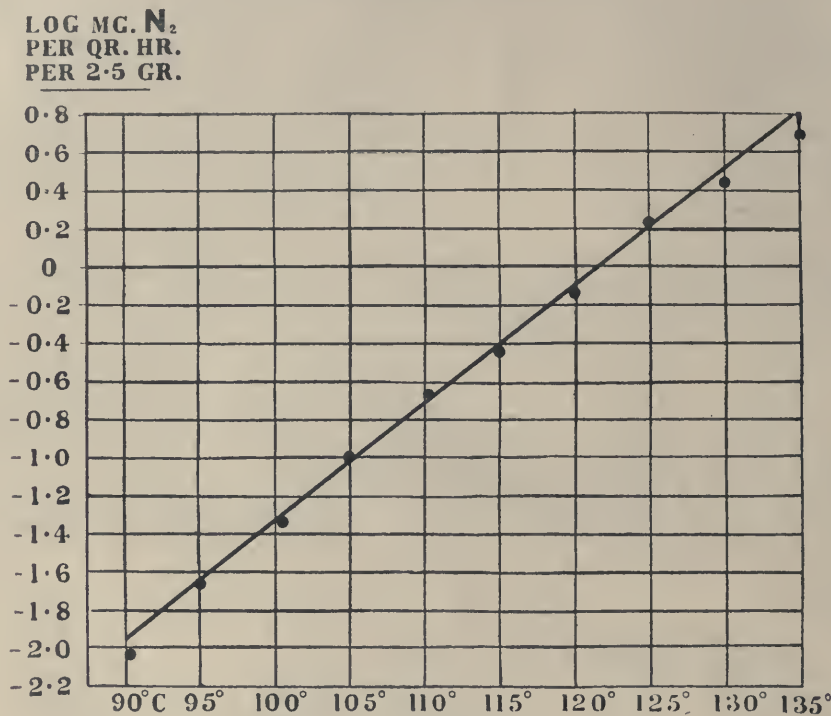


FIG. 3.—Nitrogen from Nitroglycerin, 90° to 135° C.

3. The rate of decomposition is a function of the temperature, and increases from 95° C. to 125° C. at the rate of twice for .5° C.

4. Nitroglycerin has a higher rate of decomposition than guncotton (see table) under similar conditions. As the spectroscopic method is capable of estimating nitric peroxide in still smaller concentrations than those already dealt with, the manner of the decomposition of nitroglycerin at lower temperatures is being determined without having recourse to extrapolation.

THE AFFINITIES OF THE NITROGEN ATOM.

By J. C. THOMLINSON, B.Sc.

THE suggestion given in a paper (*Science Progress*, Jan., 1909) that oxygen may in some way be compared with carbon with its affinities placed in a somewhat similar way to those of the carbon atom, generally regarded as acting at the four corners of a tetrahedron, calls for some comparison with a pentavalent value I ascribe to oxygen in dealing with the oxides of nitrogen (*CHEMICAL NEWS*, 1907, vol. xciv.).

I from thermo-chemical grounds ascribed to the three oxides of nitrogen the following structural formulæ:—



Nitrous oxide is the most stable of these, nitric oxide east so, and nitrogen dioxide intermediate.

It will at once be seen how these formulæ agree with Mr. Armstrong's views that the greatest stability occurs where the angles between the affinities of the atoms are reduced by these affinities coming more nearly into parallel.

I might further exemplify these views by saying that gypsum (calciumsulphhydrate), $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, might be

expressed as existing in solution according to the formula $2\text{CaSO}_4 \cdot \text{H}_2\text{O}_3 \cdot \text{H}_2\text{O}$. Thus at the temperature of 107° C. the crystals of gypsum melting in their own water of crystallisation might contain two molecules of calcium sulphate and one of hydrone floating in liquid trihydrone.

ANHYDROUS HYDRONITRIC ACID.*

I.—ELECTROLYSIS OF A SOLUTION OF POTASSIUM TRINITRIDE IN HYDRONITRIC ACID.

By A. W. BROWNE and G. E. F. LUNDELL.

(Concluded from p. 257).

Details of the Electrolytic Experiments.

Experiment 1.—Four and one-half grms. of potassium trinitride, corresponding to 2.4 grms. of the anhydrous acid, were introduced into the generator. To the liquefied hydronitric acid was added 0.05 gm. of dry potassium trinitride, a part of which soon went into solution, as was subsequently indicated by the formation of a crystalline residue around the upper surface of the liquid after some evaporation had taken place. The solution was subjected to the action of the electric current at temperatures varying from about 0° to -80°, with the result that an evolution of gas was observed to take place at both electrodes. The experiment was of a purely qualitative nature.

Experiment 2.—Five grms. of potassium trinitride were used in the generator, and 0.03 gm. in the electrolytic cell. The electrolysis was continued through a period of over three hours, during which time the graduated tubes were partially filled thirty-four times. The cell was maintained at a temperature of 0° throughout this experiment,

* Reported at the Thirty-eighth General Meeting of the American Chemical Society, held at New Haven, Conn., June 30th to July 2nd, 1908. From the *Journal of the American Chemical Society*, xxxi., No. 4.

and a current of about 3 milliamperes was passed through the solution. The successive readings of the gas volumes indicated the ratio of nitrogen to hydrogen to be in the neighbourhood of three to one. The total volume of gas liberated at the anode was 15.9 cc.; the total volume at the cathode was 5.4 cc.

Experiment 3.—Five grms. of potassium trinitride were used in the generator, and 0.03 gm. in the cell. The electrolysis covered a period of about four and one-half hours, and the cell was kept at a temperature considerably below 0°, but always above -80°. A current of about 7 milliamperes was employed. At one time the cathode became covered with a white solid, in all probability potassium trinitride, which for a time greatly hindered the passage of the current. Analysis of the gases obtained at the electrodes showed that 22.7 cc. of nitrogen were liberated at the anode, and 9.0 cc. of hydrogen at the cathode. This corresponds to a ratio of 2.52 to 1. In this experiment, and also in Experiment 2, it was noticed that the surface of the mercury in the anode burette (Fig. 1) was corroded. In neither case was a similar corrosion noted in the cathode burette. Two possible explanations may be offered in attempting to account for this phenomenon:—(1) Small quantities of ozone may have been formed at the anode, as a result of the possible presence of traces of moisture in the hydronitric acid; (2) small amounts of a polymeric form of nitrogen may have been formed.

Experiment 4.—Five grms. of potassium trinitride were used in the generator, and 0.03 gm. in the cell. The duration of the electrolysis was over two hours, during which time the tubes were partially filled twenty-two different times. The temperature was held as nearly as possible at -80°, and a current of about 7 milliamperes was passed through the cell. The successive readings of the gas volumes indicated the average ratio of nitrogen to hydrogen to be 2.43 to 1. One very peculiar phenomenon observed throughout this experiment was the sudden liberation of numerous small bubbles of gas in the anode tube, whenever it was refilled with hydronitric acid. This seemed to take place as the result of the slight increase in temperature to which the acid was subjected whenever it was forced up into the tube, which was never cooled to a temperature quite as low as that of the lower part of the cell. This spontaneous evolution of gas was not observed in the cathode tube, except when the acid in this tube was raised so high that a part of the liquid previously located in the neighbourhood of the anode was drawn up. Three possible explanations may be offered:—(1) Small quantities of ozone may have been formed, and may have decomposed a part of the hydronitric acid, with liberation of gas, when the temperature was very slightly raised; (2) appreciable amounts of nitrogen gas may possibly have remained in solution in the electrolyte at -80°, and may have been liberated at slightly higher temperatures; (3) small amounts of a polymeric form of nitrogen, soluble in hydronitric acid, comparatively stable at -80°, but decomposable at slightly higher temperatures, may possibly have been formed.

Experiment 5.—Five grms. of potassium trinitride were used in the generator, and 0.03 gm. in the cell. The electrolysis was conducted at a temperature of about -80°, without making any effort to read the volume of the gases liberated. When the passage of the current through the cell was discontinued, and the temperature of the electrolyte permitted to rise gradually, a spontaneous evolution of gas was noticed throughout the body of the liquid. After a current of about 7 milliamperes had been again passed through the cell at -80° for some time, the circuit was broken, and 5 cc. of an aqueous solution of potassium iodide were introduced into the cell. A small quantity of iodine, shown by subsequent titration to be equivalent to two drops of tenth-normal solution of sodium thiosulphate, was liberated.

Experiment 6.—The conditions prevailing in Experiment 3 were approximately duplicated, except that a

current from two to three times as large was employed. Toward the close of the experiment the temperature of the cell was allowed to rise to about 20°. The tubes had just been filled, and the electrolysis was apparently proceeding as usual, when a deafening explosion, accompanied by a clearly perceptible flash of light, took place, with the result that all glass apparatus in the neighbourhood of the cell was reduced to an almost impalpable powder. In spite of the extreme violence of the explosion, however, no serious personal injury was experienced by the investigators, both of whom happened to be standing, with faces protected only by goggles, within about three feet of the cell.

Experiment 7.—Ten grms. of potassium trinitride were introduced into the generator, and 0.2 gm. into the cell. The electrolysis covered a period of about two hours, during which time thirty-four readings were made. The temperature was held at 0°, and a current of from 11 to 17 milliamperes was employed. The successive readings of the gas volumes indicated a ratio of somewhat less than 2:1. No particular emphasis can be laid upon this experiment, although it was duplicated with substantially identical results, on account of the fact that the platinum electrodes used were found to contain appreciable amounts of iron. The liquid gradually assumed a reddish tint, without doubt due to the formation of ferric trinitride, and on evaporation left a very explosive solid residue of a dark red colour.

Experiment 8.—Seventeen grms. of potassium trinitride were used in the generator, and 0.2 gm. in the cell. The electrolysis was continued through a period of six hours during which time seventy readings were made. The cell was kept at a temperature of 0°, and a current of about 7 milliamperes was employed. Analysis of the gases obtained at the electrodes showed that 15.98 cc. of nitrogen (corrected) were liberated at the anode, and 5.22 of hydrogen (corrected) at the cathode, corresponding to a ratio of 3.06 to 1. The residue left after removal of the hydronitric acid from the cell was found to contain appreciable amounts of ammonia, but no hydrazine.

Experiment 9.—Seventeen grms. of potassium trinitride were used in the generator, and 0.2 gm. in the cell. Over eighty readings were made during the seven hours devoted to the electrolysis. A current of about 6 milliamperes was passed through the cell, which was kept at a temperature in the neighbourhood of -80°. The corrected volume of the gases evolved were shown by analysis to be as follows:—Nitrogen, 21.87 cc.; hydrogen, 7.41 cc. The ratio is consequently 2.95 to 1. The successive readings of the gas volumes, however, indicated throughout the entire experiment a ratio of about 2.5 to 1. This discrepancy is probably to be explained by the fact that a spontaneous evolution of gas, similar to that noted in Experiment 4, was observed throughout the present experiment. This evolution took place chiefly during the intervals between the reading of the gas volume and the transfer of the gas to the pipette, and consequently the gas evolved was not taken into account in the successive readings. Appreciable amounts of ammonia were formed during the electrolysis, but no indication of the formation of hydrazine was obtained. The amount of copper precipitated on the voltameter cathode was 0.0239 gm., corresponding to 0.0316 gm. of nitrogen and to 0.000758 gm. of hydrogen. The actual weight of nitrogen and hydrogen obtained in the experiment was 0.0275 gm. and 0.000666 gm. respectively.

Experiment 10.—For the purpose of investigating the results obtainable with a comparatively high current density at the anode, the electrolytic cell was remodelled as follows:—The pipettes, stop-cocks, and graduated tubes (Fig. 3) were replaced by simple glass tubes, one in each arm of the U-tube, reaching just to the surface of the liquid hydronitric acid, and connected above with a chain of Muencke gas wash-bottles containing concentrated sulphuric acid. At a distance of about 3 cm. below each of the side-tubes *s* and *s'*, was attached another tube, bent at an angle of 90°, and extending downward along the

side of the U-tube for a distance of a few centimetres. Each of these tubes reached to the bottom of a small test-tube, about 3 cm. long and 1 cm. in diameter, which was provided with a tight-fitting two-hole cork. Through the second opening in each cork passed a glass tube connected with a suction pump. A platinum wire of 0.3 mm. diameter served as the anode, and a piece of platinum foil 1.0 cm. long and 0.5 cm. wide was used for the cathode. The average current density at the anode amounted to about 7.7 amperes per sq. dcm. Thirteen grms. of potassium trinitride were used in the generator, and about 0.3 gm. in the cell. The test-tubes were filled with an aqueous solution of potassium iodide, and the cell was cooled with the aid of liquid air to a temperature of about -80° . A fairly rapid current of dry air was now drawn over the hydronitric acid and through the test-tubes in order to test for the presence of any volatile oxidising agent formed during the experiment, and the circuit was closed. For about one-half hour the electrolysis proceeded without accident. At the end of this time, however, since it became necessary to make a slight adjustment of one part of the accessory apparatus, the passage of the current was discontinued. No sooner had the cell been barely touched with the hand of the operator than a frightful explosion took place which completely demolished the apparatus and shattered two window-panes at a distance of about two metres from the cell.

Experiment 11.—Thirteen grms. of potassium trinitride were used in the generator, and about 0.2 gm. in the cell. An exact duplicate of the apparatus described in the preceding experiment was used, and the same conditions were chosen. Mercury was placed in the test-tubes instead of the solution of potassium iodide, and the tubes were cooled to a temperature in the neighbourhood of the freezing-point of mercury. The electrolysis proceeded without mishap for about four hours, at the end of which time the cell exploded as before, but this time without any apparent cause. The temperature throughout the experiment was held at -80° , and, moreover, at the time of the explosion part of the hydronitric acid was in the solid state.

It has been found by repeated experiments performed during the course of the present research that hydronitric acid at room temperature or even at its boiling-point may be subjected to considerable mechanical disturbance without great danger of explosion. Fairly rapid currents of air have many times been blown through the liquid, and the cell has been subjected to a series of light shocks without causing any explosion. That the substance after electrolysis at -80° should be so extremely sensitive to shock seems to point toward the possible accumulation in the cell of a very explosive compound, perhaps a polymer of nitrogen, during the electrolysis.

Summary.

In the present investigation it has been shown that—

1. Hydronitric acid, like hydrazine and ammonia, in the pure, anhydrous condition offers a remarkably high resistance to the electric current.
2. The introduction of dry potassium trinitride very greatly increases the conductivity of the anhydrous acid.
3. When a solution of potassium trinitride in hydronitric acid is electrolysed, the ratio of nitrogen to hydrogen evolved is approximately 3:1, but is somewhat lower under certain conditions. Appreciable amounts of ammonia are obtained during the electrolysis, but no hydrazine is formed.

4. Certain peculiar phenomena are observed in connection with the electrolytic experiments, which may perhaps be explained on the assumption that traces of ozone are formed, but which might possibly be attributed to the formation of small amounts of nitrine, a polymeric modification of nitrogen.

Further work along several different lines suggested by these experiments is now in progress in this laboratory.

The authors take pleasure in expressing their gratitude to Mr. T. W. B. Welsh, of the Department of Chemistry,

for considerable assistance in carrying out some of the experimental work described in this article, and to Prof. E. M. Chamot and Mr. D. S. Pratt, of the same Department, for microchemical work connected with certain parts of the research.

RAPID ELECTRO-ANALYSIS WITH STATIONARY ELECTRODES.

By JOHN T. STODDARD.

IN the interesting development, during the last few years, of methods for the rapid precipitation of metals by the electric current, the efficiency of cathodes of gauze, and of mercury with stationary anodes seems to have been largely overlooked. General attention was directed in 1903 to the fact that electro-analysis could be made in much less than the usual time by using stronger currents with rotating electrodes. Gooch and Medway (*Am. Journ. Sci.*, 4th Series, xv., 320) rotated the cathode, Exner (*Journ. Am. Chem. Soc.*, xxv., 896), the anode; and since that time much work has been published on the use of the rotating anode with dish, gauze, and mercury cathodes. The agitation of the solution, which is apparently the chief function of the rotating electrode, has also been accomplished by rotation of the solution while the electrodes are stationary—recently by Frary (*Zeit. Elektrochemie*, 1907, xxiii., 308) through the clever use of a solenoid. Rotation has come to be regarded as the essential feature of rapid electro-analytical procedure.

The experiments described in this paper show that rotation is not essential; that similarly rapid results can be obtained with stationary electrodes and no agitation of the solution beyond that produced by the heating effects and gas-evolution caused by the strong currents employed.

1. The Gauze Cathode with Stationary Anode.

In July, 1899, Cl. Winkler (*Ber.*, xxxii., 2192) published a brief paper on "Die Elektrolytische Metallfällung unter Anwendung von Elektroden aus Platindrahtgewebe," in which he stated that with a cathode of platinum gauze good deposits of a number of metals could be obtained when higher current densities than usual were employed; and that the time of precipitation was reduced to one-fourth of the usual time. The efficiency of the gauze was ascribed to the utilisation of the entire surface and to the fact that the deposited metal closes on itself around each wire of the mesh, and thus adheres better than on a plane surface. Winkler records the use of a current of 0.5 ampere, and calculates the current density as $D_{100} = 5.1$ amperes. From the data which are given, it is evident, however, that an error was made in the calculation of the gauze surface; and instead of being 9.8 sq. cm., it was about 66 sq. cm., so that the current density was only about 0.76 ampere. It may be that this fact is in part responsible for the slight interest which this suggestion for more rapid precipitation seems to have aroused.

Gauze cathodes were immediately tried in this laboratory, and it was soon evident that much more rapid precipitation than that reported by Winkler could be effected by the use of stronger currents; and, on the appearance of Gooch and Medway's paper (*loc. cit.*), a few experiments were made which showed that copper was deposited on gauze with a stationary anode in about the same times as those given for the rotating cathode. No careful study of the matter was, however, made until recently.

The cathodes employed are cylinders of platinum gauze, 3 cm. in diameter and 3 cm. long. The gauze is that described by the maker as "52-mesh" (to the inch), and the cathode is calculated to have a total surface of about 40 sq. cm.

The weight of the cathodes is about 12 grms. each; they might, however, be considerably lighter, as the wire which serves as the frame of the cylinder and for connecting

TABLE I.

Metal	Approximate weight. Grm.	Current. Amperes.	Colourless in minutes.	Complete precipitation, minutes.
Cadmium ..	0.42	5	—	15
Copper ..	0.5	6	5	10
Copper ..	0.5	8	4.5	8
Nickel ..	0.34	6	5	8
Nickel ..	0.40	6	8	12
Nickel ..	0.6	6	10	16
Silver ..	0.25	1—1.5	—	10
Silver ..	0.5	1	—	17
Zinc (NaOH) .	0.5	4	—	15
Zinc (NaOH) .	0.4	8	—	10
Zinc (KCN) ..	0.5	6	—	30

TABLE II.

Metal.	Volume of solution. Cc.	Approximate weight. Grm.	Current. Amperes.	Colourless in minutes.	Complete precipitation, minutes.
Cadmium ..	30	0.25	7—5	—	10
Cadmium ..	25	0.21	5	—	10
Copper ..	15	0.3	3—4	5	10
Copper ..	20	0.4	4	6	8
Nickel ..	15	0.36	5.5	6	10
Nickel ..	25	0.5	7	10	15
Silver ..	20	0.4	8—7.3	—	6
Silver ..	25	0.5	4.8	—	8
Silver ..	25	0.5	5.8—6.5	—	7
Zinc ..	20	0.2	8—7	—	10
Zinc ..	25	0.5	6	—	15

TABLE III.—Determinations of Metals made with Stationary Anode.

Solution taken.	Vol. of electrolyte. Cc.	Cathode used.	Current. Amperes.	Time. Minutes.	Metal found. Grm.	Metal in 1 cc. solution. Mgrms.
25 cc. Cd(NO ₃) ₂ ..	50	Gauze	5—4.5	15	0.2132	8.528
25 " " ..	25	Mercury	5—6	10	0.2124	8.496
25 cc. CuSO ₄ ..	50	Gauze	4	20	0.4944	19.776
25 " " ..	50	Gauze	6	13	0.4943	19.772
20 " " ..	50	Gauze	6	8	0.3955	19.775
15 " " ..	15	Mercury	3—4	10	0.2963	19.753
20 " " ..	20	Mercury	4	8	0.3954	19.770
25 cc. NiSO ₄ ..	50	Gauze	6	12	0.4897	19.588
15 " " ..	15	Mercury	5—5	10	0.2936	19.573
25 " " ..	50	Gauze	6	18	0.5986	23.944
15 " " ..	15	Mercury	5.5	10	0.3593	23.953
25 cc. AgNO ₃ ..	50	Gauze	1	20	0.4958	19.832
25 " " ..	50	Gauze	1	17	0.4957	19.828
20 " " ..	20	Mercury	8—7.3	6	0.3970	19.850
25 cc. ZnSO ₄ (KCN) .	50	Gauze	6	30	0.4991	19.964
25 " " ..	25	Mercury	6	15	0.4988	19.952
25 " " ..	25	Mercury	6	15	0.4989	19.956

with the electrolytic stand is unnecessarily heavy (1.4 mm.). Half its weight could be saved by using wire of 1 mm. in diameter, and the weight of the cathode brought down to 7 or 8 grms.

The anodes are cylinders of platinum foil, about 0.8 cm. in diameter and 2.5 cm. long, and in the electrolysis are placed concentrically within the cathodes.

The precipitations are carried out in 80 cc. beakers with about 50 cc. of solution—a volume which, while covering the electrodes well, gives the advantage of concentration. The wires of both electrodes are bent at an angle of somewhat more than 90° so as to rest on the lip of the beaker and allow a watch-glass cover to be used conveniently. At the end of the experiment, without interrupting the current, the solution is drawn off for testing and the cathode washed with distilled water by the aid of a syphon whose end is slipped between the electrodes.

The following solutions were used:—

1. Cadmium nitrate with just enough potassium cyanide to give a clear solution.

2. Copper sulphate with 7 or 8 drops of conc. nitric acid. The solution is heated to about 60°.

3. Nickel sulphate with 1.5 grms. of ammonium sulphate and 12 to 15 cc. of conc. ammonia.

4. Silver nitrate with the least possible excess of potassium cyanide. The solution is heated nearly to boiling.

5. Zinc sulphate with an excess of sodium hydroxide; or with sodium hydroxide to partial solution of the precipitate and then just enough potassium cyanide to give a clear solution. The solution is heated.

With the exception of silver, the character of the deposited metal is scarcely affected by the strength of

current used. With silver, if the current exceeds 1.5 amperes the deposit is yellowish, and with much stronger currents becomes voluminous and closes the mesh; with less than 1.5 amperes the precipitated silver is white and fine.

The sodium hydroxide solutions of zinc give deposits which after a time fill the mesh, but which give quantitative results. A much finer deposit is obtained from the cyanide solution, but the precipitation is somewhat slower.

As the strong currents heat the solutions, often to boiling, the preliminary heating is perhaps not necessary. In some cases, notably with the nickel solutions, so much frothing sometimes occurs that it is necessary to reduce the current. This necessity may be avoided by the use of a deeper beaker.

The metals were completely precipitated in times which are given in Table I. The current density is not given; D_{100} is in all cases equal to the current noted divided by 0.4. The fall of potential between the electrodes is also omitted as it has little significance; it is only necessary to have at command sufficient voltage to deliver the required current through the electrolytic cell. In these experiments a storage battery of ten cells in series was employed.

Some determinations on both gauze and mercury cathodes are given at the end of this paper.

II. The Mercury Cathode with Stationary Anode.

When the use of the mercury cathode proposed by Wolcott Gibbs, in 1880, was taken up at the University of Pennsylvania (*Journ. Am. Chem. Soc.*, xxv., 884), stationary anodes were at first employed, with comparatively low currents and correspondingly long times

for precipitation—over-night determinations; but in 1904—1905 Kollock and Smith (*Ibid.*, xxvii., 1255) introduced the use of the rotating anode with the mercury cathode, and found that with strong currents the metals were precipitated in astonishingly short times.

While studying the efficiency of the gauze cathode, as described in the first part of this paper, the suggestion occurred that the heating and gas-evolution produced by strong currents should so effectually agitate the solution used with the mercury cathode as to make the rotation of the anode unnecessary for rapid precipitation in a cathode material in which the metal dissolves. Though it seemed very unlikely that the combination of mercury cathode, stationary anode, and strong current had not been tried, and, if so, rejected for some good reason, the experiment was made; and it proved that, under these circumstances, cadmium, copper, nickel, silver, and zinc (and presumably other metals) were precipitated in times which are at least comparable with those reported for the rotating anode.

The procedure is essentially that described by E. F. Smith in the fourth edition of his "Electro-Analysis."

A 45—50 cc. beaker is used with about 40 grms. of mercury, and an anode consisting of a flat spiral of platinum wire placed 0.5 to 1 cm. from the surface of the mercury. The electrode wires are bent as in the case of the precipitations on gauze so that a watch-glass cover may be used. At the end of the precipitation, the solution is syphoned off for testing, and the mercury washed with distilled water by the aid of the syphon, without interrupting the current, until the latter drops to about zero. The mercury is again washed with water, then with alcohol, and finally with ether, and dried at a very gentle heat.

The solutions used in testing the efficiency of the method were the nitrates of cadmium and silver, and the sulphates of copper, nickel, and zinc. Five or six drops of sulphuric acid (1:4) were added in each case except that of silver, where the same amount of nitric acid was used. The silver solution becomes black as soon as the current is closed, from finely divided "peroxide," but clears again in three or four minutes. All the solutions are rapidly heated by the currents employed, and the only limit to the strength of current which can be used is that indicated by possible loss from too violent boiling.

Table II. shows in what times complete precipitation takes place.

In Table III. some determinations are given with gauze and mercury cathodes from the same solutions of the salts, and, for the sake of ready comparison of the results, there is added the weight of metal in one cubic centimetre of the solution, calculated from the weight found.

Summary.

It is shown in this paper that cadmium, copper, nickel, silver, and zinc (and probably other metals) can be precipitated from their solutions, completely and in weighable condition, by strong currents with the use of stationary electrodes, in substantially the same times as those required when rotating electrodes are employed.

The advantages of this are obvious; it means a return to the simplicity of apparatus and manipulation of the older and slower methods, while retaining the speed of the new. It should lead to the introduction of rapid methods of electro-analysis by those who have hesitated to employ them on account of the initial extra expense and the use of the machinery necessary for rotation.—*Journal of the American Chemical Society*, xxxi., No. 3.

α -Oxalglutaric Ether. α -Keto adipic Acid.—H. Gault.— α -Oxalglutaric ether is formed by condensation in an ethereal medium of one molecule of oxalic ether and one molecule of glutaric ether in presence of sodium ethylate. In alcoholic solution the same reaction does not occur. α -Oxalglutaric ether saponifies very easily, the product being α -keto adipic acid, which yields both acid and ketone derivatives. Thus it combines with hydroxylamine to give an oxime.—*Comptes Rendus*, cxlviii., No. 17.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, May 27th, 1909.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"Notes concerning Tidal Oscillations upon a Rotating Globe." By Rt. Hon. Lord RAYLEIGH, O.M., F.R.S.

"The Absolute Value of the Mechanical Equivalent of Heat in terms of the International Electrical Units." By Prof. HOWARD T. BARNES, D.Sc., Macdonald Professor of Physics, McGill University, Montreal.

It is pointed out that the Clark cells used by the author in his determinations of the mechanical equivalent of heat in terms of the electrical units were prepared according to the old specifications. The absolute measurements of the Clark cell now being carried on with such precision in the various standardising laboratories are expressed in terms of the new form of cell with specially prepared mercurous sulphate. There is an important difference between the cells, which Wolff and Waters has shown amounts to 0.30 millivolts. The author has compared a set of modern cells with cells set up according to the old specifications, and finds the same constant difference. Taking 1.4330 int. volts at 15° C. as representing the modern cells, then the cells made by the old specifications must be taken as 1.4333 int. volts at 15° C.

The author's measurements of the mechanical equivalent at different temperatures were calculated on the basis of a value for the Clark cell equal to 1.4342 int. volts at 15° C. Re-calculating on the new basis, the value of the mean calorie is found to be 4.1849 joules. This agrees with Reynolds and Mooreby's directly determined mean which, expressed accurately for an interval of temperature between 0° and 100° C., comes to 4.1836 joules. Rowland's mean value between 5° and 35° C. is 4.185 joules, while the author's value between the same limits of temperature is 4.1826 joules. Thus assuming the variation of the specific heat of water to be correctly determined, the value of the Clark cell, equal to 1.4330 int. volts, brings the electrically determined mechanical equivalent into excellent agreement with the same constant measured by mechanical means.

"An Approximate Determination of the Boiling-points of Metals." By H. C. GREENWOOD.

Although high temperatures can now be easily attained by means of electric heating, no general investigation of the boiling-points of metals has yet been carried out. Moreover, such values as are available have in most cases been deduced indirectly and are very discordant. In the present investigation, apparatus was devised for directly measuring the temperatures of ebullition under atmospheric pressure of a considerable number of metals, allowing of use up to 2700° C. Heating was effected electrically, and the metal, when unaffected by carbon, was contained in a thin-walled graphite crucible on the outside of which the temperature was estimated by means of a Wanner optical pyrometer. The difference in temperature between the internal and external surfaces of the crucible walls was found to be negligible. Accuracy of the temperature measurements was secured by checking the pyrometer against the "black body" melting-points of specially purified strips of platinum, rhodium, and iridium.

The following values were found:—Aluminium, 1800° C.; antimony, 1440° C.; bismuth, 1420° C.; chromium, 2200° C.; copper, 2310° C.; iron, 2450° C.; magnesium, 1120° C.; manganese, 1900° C.; silver, 1955° C.; tin, 2270° C. In dealing with the metals aluminium, chromium, iron, and manganese, which readily combine with carbon, considerable difficulty was experienced in avoiding contact with carbon at the high temperatures in question. This was finally accomplished by the use of graphite crucibles brasqued with previously fused magnesia. In the absence

of this protective lining the boiling-point was very greatly modified by carburisation. The temperatures indicated for aluminium and manganese were far below those hitherto supposed necessary for ebullition.

"Some Results in the Theory of Elimination." By A. L. DIXON.

"Liquidus Curves of the Ternary System Aluminium-copper-tin." By J. H. ANDREW, M.Sc., and C. A. EDWARDS.

The study of the constitutions of alloys is of great theoretical interest and of some practical value; in fact, it may be said that the heat-treatment of a given series of alloys cannot be correctly accomplished without an accurate knowledge of the structural changes which occur with varying temperature and concentration. We are now in possession of accurate data bearing on the constitution of a large number of alloys containing only two elements, but very little work has been published on mixtures of three or more metals.

The object of the present research was to throw some light on the properties of ternary alloys, and, incidentally, the effect of impurities on binary alloys.

The metals from which the alloys were made had the following degree of purity:—

Aluminium	99.57 per cent
Copper	99.98 "
Tin	99.98 "

Freezing-point Determinations.—The freezing-points of the alloys were determined directly after mixing by means of a platinum + 10 per cent iridium thermo-junction. The free ends of the wires were connected by a mirror galvanometer and balancing arrangement similar to that described by Messrs. Carpenter and Keeling in their work on the iron-carbon alloys.

In order to locate the position of the isothermal curves more than 400 alloys and melting-point determinations were made.

Conclusions.—The character of the liquidus curves, as seen on diagram, indicates that no well-defined ternary compound is deposited from any of the liquid alloys.

The affinity of tin for either aluminium or copper is not sufficient to overcome the affinity of the last two elements for each other.

As a consequence of the above, curves of the melting-points of alloys containing a constant percentage of tin bear a striking resemblance to the liquidus curve of the aluminium-copper alloys.

Tin is insoluble in by far the greater number of the alloys.

"Studies on the Structure and Affinities of Cretaceous Plants." By Miss M. C. STOPES, Ph.D., D.Sc., F.Z.S., and K. FUJII, Ph.D.

CHEMICAL SOCIETY.

Ordinary Meeting, May 20th, 1909.

Sir JAMES DEWAR, F.R.S., Past-President, in the Chair.

MESSRS. F. P. Burt, R. C. H. Cooke, G. S. Cooper, and F. L. Usher were formally admitted Fellows of the Society.

The CHAIRMAN announced that the Council had voted the sum of £10 towards the International Memorial now being organised to commemorate the contributions of Amedeo Avogadro to chemical and physical science.

It was stated also that the Society have become indebted to the Society of Dyers and Colourists for a bronze reproduction of a plaque by Mr. F. W. Pomeroy, R.A., representing the late Sir William Perkin.

Certificates were read for the first time in favour of Messrs. John Gunning Moore Dunlop, St. Helen's, Holywood, Belfast; Oswald Farquhar Kirby, M.A., B.Sc., 14, Wellclose Mount, Leeds; Fred Robinson, B.A., B.Sc., Broadway, Skerton, Lancaster.

Of the following papers, those marked * were read:—

*138. "Thio-oxalates." (Preliminary Note). By HUMPHREY OWEN JONES and HUBERT SANDERSON TASKER.

The esters of dithio-oxalic acid are readily prepared by the action of alkyl hydrosulphides on oxalyl chloride; the dimethyl, diethyl, and diphenyl esters are crystalline, and show a distinct yellow colour (the diphenyl compound is a bright sulphur-yellow).

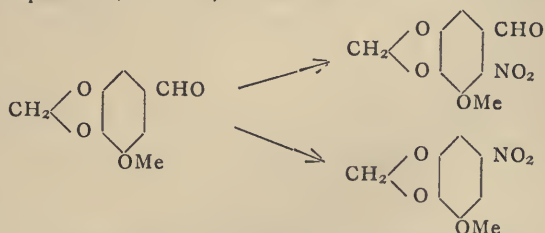
These esters are decomposed by hot potassium hydroxide solutions into potassium oxalate and alkyl hydrosulphide, but when heated with a concentrated alcoholic solution of potassium hydrosulphide a white solid separated, which was found to be potassium dithio-oxalate, (KSCO)₂. This salt is white and crystalline, and is very soluble in water, giving a yellow solution, from which it separates in colourless prisms when evaporated on the water-bath. The salt gives intense colours with solutions of certain metallic salts, and precipitates with others; some of these precipitates decompose on heating, yielding the sulphide of the metal. The most striking reactions are those given with solutions of nickel and cobalt salts; the former give an intense magenta colour, the latter a deep brown colour, in both cases so intense as to be visible in solutions containing one part of the metal in 8,000,000 parts of solution. The coloured compound formed with nickel can readily be obtained in small, black, lustrous needles, resembling small crystals of potassium permanganate; these were found to have the composition required by the formula C₄O₄S₄K₂Ni. Solutions of this salt and the cobalt salt are stable to acids, and the metals are only precipitated very slowly from them by the addition of potassium hydrosulphide or hydroxide.

Potassium monothio-oxalate is prepared by the action of alcoholic potassium hydrosulphide on diethyl monothio-oxalate, (COSEt·CO₂Et), and separates slowly in white needles, which contain one molecule of water of crystallisation. This salt is also very soluble in water, but gives a colourless solution; the solution decomposes on addition of acid, and gives colours and precipitates with metallic salts which are very similar to those given by the dithio-oxalate, but the insoluble salts are in this case more readily decomposed.

The corresponding acids are unstable, and have not yet been isolated in the pure state.

*139. "The Action of Nitric Acid on the Ethers of Aromatic Hydroxyaldehydes." By ARTHUR HENRY SALWAY.

The author has shown that when myristinaldehyde is acted on by nitric acid (sp. gr. 1.41) at 0°, part of the aldehyde is directly nitrated, whilst the remainder undergoes nitration with the elimination of the aldehyde group, the products of the reaction being nitromyristinaldehyde and 5-nitro-1-methoxy-2:3-methylenedioxybenzene. It was also shown, by determining the position of the nitro-group, that the formation of the latter compound is due to the direct substitution of the aldehyde group by the nitro-group. The action of nitric acid on myristinaldehyde is represented, therefore, as follows:—



On investigating the action of nitric acid on piperonal, vanillin methyl ether, and anisaldehyde, it was found that the above transformation is common to the ethers of aromatic hydroxyaldehydes, and that the accumulation of oxyalkyl groups in the molecule enhances the readiness with which the aldehyde group is eliminated on nitration.

DISCUSSION.

Dr. MORGAN remarked that the author's hypothesis of the formation of an additive compound with aldehyde and nitric acid preceding the replacement of the aldehyde group by nitroxyl is confirmed by the fact that aldehydes and ketones both furnish nitrates which may often be obtained crystalline. Camphor nitrate has long been known, and benzaldehyde nitrate has recently been isolated (D.R.-P. 206695 and *Abstr.*, 1909, i. 238).

*140. "Some Physical Properties of Radium Emanation." By ROBERT WHYTLAW GRAY and Sir WILLIAM RAMSAY, K.C.B.

The atomic weights of the inactive gases are:—Helium, 4; neon, 20; argon, 40; krypton, 83; and xenon, 131. The differences are respectively 16, 20, 43, and 48. Differences of 44×2 are to be found between the atomic weights of antimony and bismuth, and of barium and radium; it is therefore to be expected that the element following xenon in the Periodic Table should have the atomic weight 175; the subsequent element, 219; and possibly an element of still higher atomic weight, 263. The emanation from radium has been condensed to a liquid; its vapour pressures have been determined in a modified Andrew's apparatus, and the volume of the liquid has also been measured. The boiling-point under atmospheric pressure is -62° ; the critical temperature is 104.5° , and the critical pressure is 47.450 mm. If these numbers are mapped on segments of circles on which the corresponding constants for argon, krypton, and xenon lie, they intersect the ordinate of atomic weights at the figure 176. That appears to decide the atomic weight of the emanation; for if it be assumed as 219, the form of the curve would have to be completely altered, and, indeed, would become reflex. From another standpoint, the boiling-point, with atomic weight 219, would be 49 degrees higher, and the critical point 53 degrees higher, than the points where the atomic weight ordinates cut these curves.

DISCUSSION.

Sir WILLIAM RAMSAY added the following particulars to Dr. Gray's description of the results of their experiments:—The volume of the emanation, calculated for 0° and 760 mm. pressure, is 0.6 cub. mm. per grm. of radium in radioactive equilibrium; this confirms Rutherford's measurements. The sudden diminution of the volume of the emanation, remarked by himself and Soddy, again with Cameron, and by Rutherford, is due in all probability to the absorption of the foreign gas by the walls of the containing vessel under the influence of the emanation. It has been observed, too, that emanation also enters the walls of the tube. In Mr. Usher's experiments with ammonia, hydrogen disappeared, and was subsequently recovered from the broken-up tube by heating it in a vacuum.

*141. "Isolation and Synthesis of *p*-Hydroxyphenylethylamine, an Active Principle of Ergot soluble in Water." By GEORGE BARGER.

The isolation of *p*-hydroxyphenylethylamine, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$, from aqueous ergot extracts, and the synthesis of this physiologically active principle by the reduction of *p*-hydroxyphenylacetone nitrile, were described.

*142. "Nitrotetramethyldiphenyl." (Preliminary Note). By ARTHUR WILLIAM CROSSLEY and CHARLES HERBERT HAMPSHIRE.

When fuming nitric acid is gradually added to *o*-xylene, there are obtained unchanged *o*-xylene, mononitro-*o*-xylenes, and a nitrotetramethyldiphenyl, $\text{C}_{16}\text{H}_{17}\text{O}_2\text{N}$ (*Trans.*, 1909, xcv., 217), crystallising from alcohol in clusters of stout, yellow, flattened needles, melting at 115° .

That the two benzene nuclei in this substance are linked together by carbon atoms of the nuclei and not by those of the methyl groups is proved by oxidation with dilute nitric acid, when a nitrotetracarboxylic acid, $\text{C}_{12}\text{H}_5\text{O}_2\text{N}(\text{CO}_2\text{H})_4$, is produced. It crystallises from water with H_2O in small, white clusters of hair-like

needles, melting and evolving gas at 225° . The tetraethyl ester, $\text{C}_{12}\text{H}_5\text{O}_2\text{N}(\text{CO}_2\text{Et})_4$, crystallises from alcohol in almost colourless, transparent, irregular needles, melting at $126-127^\circ$.

Nitrotetramethyldiphenyl is reduced by tin and hydrochloric acid to aminotetramethyldiphenyl, which separates from light petroleum in radiating clusters of transparent needles, melting at 81° .

Experiments are now in progress with the object of definitely establishing the exact positions of the various groups in this nitrotetramethyldiphenyl.

143. "Ammonium Perhalides." By FREDERICK DANIEL CHATTAWAY.

The author has recently (*Proc.*, 1908, xxiv., 172) expressed the view that the diazonium trihalides are N-trihalogen derivatives of the hydrazines. In order to compare their properties with those of the ammonium perhalides, the latter have been prepared and their behaviours studied. Only ammonium perbromide, ammonium periodide, and ammonium dibromiodide have apparently been previously isolated. The supposed risk of explosion from liberation of nitrogen chloride appears to have hindered attempts to prepare the perhalides containing chlorine. Two of these compounds have now been prepared, and prove to be remarkably stable substances. Ammonium dichloriodide, $\text{NH}_4\cdot\text{Cl}_2\text{I}$, crystallises in large, brilliant scarlet prisms, and ammonium chlorobromiodide, $\text{NH}_4\cdot\text{ClBrI}$, in large, brilliant garnet-red prisms. Both can be kept in closed vessels for a long period without apparent change. When heated they do not explode, but lose two atoms of halogen, pure ammonium chloride being left. Both are extremely soluble in water, and deliquesce in damp air.

A study of the properties of the ammonium perhalides shows that they and the diazonium perhalides cannot be regarded as analogously constituted. For example, diazobenzene perbromide is a solid insoluble in water which can be preserved in a vacuum over lime for a long period with very slight loss in weight. Ammonium perbromide, on the other hand, is extraordinarily easily soluble in water, and loses two-thirds of its bromine if exposed for a few minutes in the air.

A large number of perhalides of primary amines have been prepared; these closely resemble the ammonium perhalides in properties.

144. "Studies in Asymmetric Synthesis. Part VIII. The Asymmetric Synthesis of *l*-Mandelic Acid." By ALEX. MCKENZIE and HERBERT BROOKE PERREN HUMPHRIES.

The authors described the asymmetric synthesis of *l*-mandelic acid. *l*-Menthyl benzoylformate was reduced by aluminium amalgam, the reduction product acetylated, and a laevorotatory mandelic acid mixture obtained by hydrolysis of the reduction product and subsequent complete elimination of the active menthol.

The isomeric *l*-menthyl acetylmandelates have also been investigated.

145. "Note on the Condensation of Acetone and Hippuric Acid." By WILLIAM HENRY PERKIN, jun., and JOHN LIONEL SIMONSEN.

Hippuric acid and acetone readily condense in the presence of acetic anhydride and sodium acetate with formation of the anhydride of α -benzoylamino- β -dimethylacrylic acid,

$\text{CMe}_2\cdot\text{C} \begin{array}{c} \diagup \text{N}=\text{CPh} \\ \diagdown \text{CO}\cdot\text{O} \end{array}$, which crystallises from dilute

alcohol in almost colourless needles, m. p. $98-99^\circ$. When hydrolysed with alkalis or cold hydrochloric acid, it is converted into α -benzoylamino- β -dimethylacrylic acid, $\text{CMe}_2\cdot\text{C}(\text{NH}\cdot\text{COPh})\cdot\text{CO}_2\text{H}$, which separates from ethyl acetate in glistening needles decomposing at 217° . This acid, when heated with concentrated hydrochloric acid, is decomposed into benzoic acid and dimethylpyruvic acid, $\text{CHMe}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$. Dimethylpyruvic acid, which has not previously been obtained in a pure state, solidifies, when cooled, to thin leaflets melting at about 16° , and boils at

133–135°/200 mm. It yields an oxime decomposing at 161°, a semicarbazone decomposing at 176°, and a hydrazone decomposing at 152° (not 129° as stated by Brunner, *Monatsh.*, 1895, xv., 763). Its ethyl ester boils at 173°/764 mm.

The authors wish to reserve this acid for further investigation.

146. "The Physical Properties of Aqueous Sodium Sulphite." By HAROLD HARTLEY and WILLIAM HENRY BARRETT.

In a systematic examination of the system sodium sulphite-water, the solubility of the two stable forms $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ and Na_2SO_3 has been determined, and a transition temperature has been found in the neighbourhood of 22°. The conditions under which either the hydrated modification or ice separates from a supersaturated solution have been studied; the extent of the metastable region in the former case amounts to as much as 30°. The crystallographic properties of the anhydrous salt have also been examined.

147. "The Preparation of Disulphides. Part V. Diethyl esters of α -Dithiodibutyric, α -Dithiodiisobutyric, and α -Dithiodiisovaleric Acids." By THOMAS SLATER PRICE and DOUGLAS FRANK TWISS.

In continuation of previous work the diethyl esters of α -dithiodibutyric, α -dithiodiisobutyric, and α -dithiodiisovaleric acids have been prepared by the electrolytic reduction of the mixtures obtained by the interaction of sodium thiosulphate with ethyl α -bromobutyrate, ethyl α -bromoisobutyrate, and ethyl α -bromoisovalerate respectively. These esters are all liquids heavier than water and distil unchanged under diminished pressure; the boiling-points are as follows:—Diethyl α -dithiodibutyrate, 187°/22 mm.; diethyl α -dithiodiisobutyrate, 166°/19 mm.; diethyl α -dithiodiisovalerate, 173°/12 mm.

From these esters only α -dithiodiisobutyric acid could be prepared in a pure state; it is a solid, melting at 197–198°.

148. "Relation between Chemical Constitution and Physiological Action in the Tropeines." Part II. By HOOPER ALBERT DICKINSON JOWETT and FRANK LEE PYMAN.

In continuation of former work on the subject, the authors have prepared and submitted to physiological examination a large number of tropeines, many of which had not been previously described. The physiological results indicated that the so-called Ladenburg's generalisation (which is not due to Ladenburg) cannot be strictly applied.

149. "The Formation of Silicates, Glasses, and Glazes." By JOHN W. COBB.

On the assumption that a glass can be regarded as formed by the combination and solution of its constituent oxides, the author has studied the process of formation of the glass represented by the formula $\text{Na}_2\text{O} \cdot \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{SiO}_2$.

An investigation on the combination of lime and silica shows that the compounds formed are $2\text{CaO} \cdot \text{SiO}_2$ and $\text{CaO} \cdot \text{SiO}_2$.

Lime and alumina interact to form the compounds $\text{CaO} \cdot \text{Al}_2\text{O}_3$, $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$, and an insoluble calcium aluminate, presumably containing a large amount of alumina.

The general question of chemical interaction between solids was discussed, and the conclusion was drawn that:—(1) The temperature of formation of a slag and its fusion point are not identical, nor are they apparently related (in opposition to Boudouard's generalisation); (2) interaction between solids may go far, even to completion, without fusion; (3) from 800° upwards the state of mixed solid particles is one of fairly effective molecular contact, allowing free play to selective chemical affinities.

150. "The Determination of the Rate of Decomposition of Benzenediazonium Chloride." By FRANCIS EDWARD EVERARD LAMPLUGH.

Some further experiments (compare *Trans. Camb. Phil. Soc.*, 1908, xiv., 580; *Proc.*, 1909, xxv., 24) have been made on the decomposition of benzene diazonium chloride, and direct measurements of the amount of nitrogen stored up in the solution have been obtained. When rather more than ordinary care is taken to keep the vessels and solutions free from dust and impurities, degrees of supersaturation up to 300 times the normal amount of gas dissolved have been observed.

Further experiments with direct measurement of temperature have confirmed the values of the constants previously obtained for the reaction (*Trans. Camb. Phil. Soc.*, 1908, xiv., 590).

151. "Acids as Accelerators in Acetylation." Part II. By ALICE EMILY SMITH and KENNEDY JOSEPH PREVITE ORTON.

The speed of acetylation of *s*-tribromophenol in the presence of sulphuric, perchloric, and orthophosphoric acids has been measured. Whereas in acetic acid and chloroform solution, acetic anhydride has no perceptible action on *s*-tribromophenol at the ordinary temperature, even after keeping for several weeks, in the presence of perchloric and sulphuric acids, acetylation takes place very rapidly. Orthophosphoric acid (or phosphoric oxide) comes far behind as an accelerator. When the quantity of acid is small, the rate of the reaction is approximately proportional to its concentration. Comparing gram-molecular proportions, perchloric acid is about 2.5 times as effective as sulphuric acid.

Chloroform is the medium in which acetylation is the most rapid, but acetic acid is only slightly inferior. Benzene and acetone are unfavourable to acetylation.

A comparison of pyridine, acids, and sodium acetate as accelerators of acetylation by acetic anhydride, shows that both the two former are far superior. Pyridine is approximately as effective as perchloric acid and therefore superior to sulphuric acid.

152. "Resolution of Racemic Alcohols." (Preliminary Note). By ROBERT HOWSON PICKARD and JOSEPH KENYON.

Pickard and Littlebury have recently described (*Trans.*, 1907, xci., 1973) a method for the complete resolution of racemic alcohols by the fractional crystallisation of salts formed by acid esters of the alcohol with optically active bases. By this method they obtained the pure borneols and isoborneols, and have synthesised *l*-menthol from thymol (*Proc.*, 1908, xxiv., 217).

The present authors in a similar way (*Trans.*, 1907, xci., 2058) carried out the first successful resolution of an aliphatic alcohol, namely, that of octane-2-ol with $[\alpha]_D^{20} 17 \pm 9.9$, and in view of work recently published abroad, wish to state that in conjunction with several collaborators they are engaged in applying the method to alcohols of very varied types.

Among the secondary alcohols already resolved (the specific rotatory power, $[\alpha]_D^{20}$, being given in brackets) are:—Butane-2-ol ($+13.3^\circ$); pentane-2-ol ($+14.3^\circ$); hexane-2-ol ($+11.6^\circ$); nonane-3-ol ($\pm 8.0^\circ$); phenylmethylcarbinol ($+32.8^\circ$); and phenylethylcarbinol ($\pm 27.3^\circ$).

153. "Syntheses with Phenol Derivatives containing a Mobile Nitro-group. Part II. The Interaction of 2:3:5-Trinitro-4-acetylaminophenol and Amines" (continued). By RAPHAEL MELDOLA and JAMES GORDON HAY.

In continuation of former researches (*Trans.*, 1906, lxxxix., 1935; 1908, xciii., 1659) the authors have studied the formation of iminazoles and other compounds quantitatively from the point of view of steric hindrance. The protective influence of substituents in the ortho-position is brought out very clearly in the recorded results: With the hydroxyl or methoxy-group in the para-position, some protecting influence is also exerted, the yields in the case of *p*-aminophenol and *p*-anisidine being less than with the corresponding meta-compounds. The general results obtained with the six series of isomeric substituted amines,

viz., the chloroanilines, bromoanilines, nitroanilines, amino-phenols, anisidines, and aminobenzoic acids, have been classified in the order of yield and compared with the results obtained by Wedekind with picryl chloride. Experiments with the trinitro-compound and secondary amines have revealed the remarkable fact that catenation takes place only with dimethylamine and piperidine. All the homologues of dimethylamine, from diethylamine to diisooamylamine, are without action. This fact has led the authors to suggest an extension of the hypothesis of steric hindrance to cases in which a mobile atom or radicle is protected on both sides by ortho-substituents, and in which the actual size of the radicles carried by the reacting compound determines the possibility of catenation.

All the new iminazoles and *m*-aminophenol derivatives prepared in the course of the research were described and characterised.

NOTICES OF BOOKS.

Elementary Practical Chemistry. Part II. *Analytical Chemistry.* By FRANK CLOWES, D.Sc. (Lond.), and J. BERNARD COLEMAN, A.R.C.Sc. Sixth Edition. London: J. and A. Churchill. 1909.

THE second part of this laboratory book for the use of elementary students of chemistry deals with qualitative analysis as far as the commoner metals and acid radicles are concerned. A thorough elementary course of volumetric analysis is also included, and simple gravimetric estimations are described. A useful section dealing with the preparation of various inorganic compounds and their purification by crystallisation, sublimation, &c., will provide plenty of practical work for the student, who, by the time he has worked through most of the typical exercises described, should have gained a fair amount of manipulative skill and also a practical knowledge of a large number of important metallic and non-metallic compounds. The book is already well known as a thoroughly trustworthy practical guide, and every fresh edition contains some new feature which represents an improvement either in the scheme or in the details of the work.

Sugar. A Handbook for Planters and Refiners. By the late JOHN A. R. NEWLANDS and BENJAMIN E. R. NEWLANDS, F.I.C., F.C.S. London: E. and F. N. Spon, Ltd. New York: Spon and Chamberlain. 1909.

THIS comprehensive text-book of sugar-growing and refining has for a long time been regarded as a valuable work of reference for planters and manufacturers, and the new edition, omitting obsolete matter and dealing only with modern methods, will be found in every respect a trustworthy guide. The practical rather than the scientific aspect of the subject is emphasised, and full details of refinery, plant, &c., are given. Methods of performing an analysis are described in one chapter, and the production of rum and other alcoholic spirits is treated in outline. The sugar manufacturer should regard the book as one without which his library is incomplete, and he will find that the new edition is thoroughly up to date.

Gesättigte Salzlösungen. ("Saturated Salt Solutions"). By Dr.phil. ERNST JÄNECKE. Halle-a-S.: Wilhelm Knapp. 1909.

IN this monograph a systematic summary of the solutions of various salts in water is given, the phase rule being used as the basis of classification. The monograph is to a certain extent a reproduction of the author's lectures on the subject, which were delivered in the summer of 1906 in the Technische Hochschule in Hanover. Much use is made of graphic representation, and mathematics are avoided as far as possible. The diagrams are sometimes not very clear, but, on the other hand, the wording of the explanations is admirably lucid, and a very good exposition of the Phase Rule is given in the introduction. These solutions, which contain two or more salts dissolved in water, are

represented by new diagrams which are decidedly simpler than the usual graphic representations, and in some other details the author's treatment of the subject exhibits innovations.

Die Bedeutung der Kolloide zur die Technik. ("The Importance of Colloids in Technics"). By Professor Dr. KURT ARNDT. Dresden: Theodor Steinkopff. 1909.

THE literature of colloids is growing with such rapidity that the chemist is beginning to find a difficulty in keeping pace with it, and with the amount of theoretical and practical knowledge required of him in order that he may profitably study its latest developments. Hence this book, which does not touch upon theoretical matters at all, but simply discusses from a practical point of view the importance of colloids in various branches of technics, will be acceptable to the many practising chemists who feel that the growth of the subject has left them a little behind. The nomenclature of colloid chemistry and the general properties of colloids are first outlined, and then the industries in which the colloidal substance plays an important part are treated individually. The text is based upon a lecture which the author delivered in Berlin, and which was found most illuminating and interesting by the audience, and there can be no doubt that the wider circle who will be able to become familiar with it in book form will find it equally valuable.

CORRESPONDENCE.

A METHOD OF HARMONISING THE ELEMENTS WITH MATHEMATICAL THEORY, AND THE POTENTIAL ENERGY OF THE ELEMENTS.

To the Editor of the Chemical News.

SIR,—When in October, 1906, I discovered the approximate relationship of the heats given out by the elements to their atomic weights in going into combination, I was unaware of Mr. Geoffrey Martin's book on "Thermochemistry" (reviewed in *Knowledge*).

The subject demonstrated in any manner by a wave theory does not detract from the value of an experimental proof of thermo-chemical equivalents.

Mr. Loring's paper (CHEMICAL NEWS, xcix., 148) on "Harmonising the Atomic Weights with Mathematical Theory" might lead us to quote Pattison Muir:—"Mathematical theories of physical phenomena in which the forces at work are thoroughly known are complete, and capable of making predictions which may afterwards be verified by experiment, or even of predicting phenomena which are altogether beyond the reach of experimental verification. When, however, the forces are but partly known, the theory may predict results, but cannot account for the phenomena to which it is applied."

In noting Mr. Daniel Rankin on "Potential Energy of the Elements," I may say that at that time, October, 1906, I was considering the "Total Energy of the Elements."—I am, &c.,

J. C. THOMLINSON.

Cape Chemical Society.—The Annual Meeting was held on April 30th, 1909, Dr. Chas. F. Juritz, President, in the Chair. The President laid before the Society a paper on "The Yellowing of Citrus Trees," by J. Muller, B.A., Member of the Society. Dr. R. Marlot (President-Elect) read his Presidential Address on "The Chemistry of some Vegetable Products of South Africa." The following office-bearers for 1909 were elected:—Vice-President, Chas. F. Juritz, M.A., D.Sc., F.I.C.; Hon. Secretary and Treasurer, St. Clair O. Sinclair, M.A.; Additional Members of Council, G. N. Blackshaw, B.Sc., F.C.S., and Prof. P. D. Hahn, Ph.D., M.A. The Treasurer's financial statement showed a balance in hand of £37 6s. 9d. The rules, after amendment, were passed as now printed.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlviii., No. 18, May 3, 1909.

Solidification of Mixtures of Water and Normal Butyric Acid.—H. Faucon.—Neither the fusibility curve nor microscopic examination suggests the existence of a hydrate of butyric acid. Below -3.8° water and normal butyric acid are miscible in all proportions. Above this temperature, and for concentrations varying from 25 to 60 per cent of acid, mixtures are not homogeneous. Solutions containing small quantities of acid do not exhibit a break at the eutectic temperature; only solutions containing more than 60 per cent of acid give a break at -13.4° , the eutectic temperature.

Action of Oxidising Agents on Silicochloroform.—A. Besson and L. Fournier.—At -80° mixtures of silicochloroform and dry oxygen, after exposure to sunlight, give a mixture of oxychlorides from which $\text{Si}_2\text{Cl}_6\text{O}$ can be isolated. Ozone acts very violently on SiHCl_3 , the products being $\text{Si}_2\text{Cl}_6\text{O}$ and a large proportion of oxychlorides of higher molecular weight. NO_2 has an extremely violent action on SiHCl_3 , which may be represented by the equation $\text{SiHCl}_3 + 2\text{NO}_2 = \text{SiO}_2 + 2\text{NOCl} + \text{HCl}$. Sulphuric anhydride acts slowly on silicochloroform in the cold, giving SO_2 and oxychlorides of silicon, besides sulphur oxychloride.

Influence of Colloidal State on Dyeing.—Léo Vignon.—The author has studied the action of an acid, basic, and substantive dye on two colloidal substances, starch and gelatin. The dyes used were roccellin, fuchsine, and congo-red. It was found that starch jellies behave like cotton, and gelatin jellies like wool and silk.

New Method of Isomerisation in the Terpene Series.—Géza Austerweil.—When pinene is heated under pressure to a temperature not exceeding that at which resinification commences, a good yield of optically active borneol is obtained. The pinene employed has to be absolutely free from water.

Sub-oxides of Cæsium.—E. Rengade.—The fusibility curves of mixtures of varying proportions of monoxide of cæsium and the metal show that there are at least four definite compounds containing less oxygen than the monoxide, Cs_2O . The formulæ of these compounds are Cs_7O , Cs_4O , Cs_5O_2 , and Cs_3O . Nearly pure crystals of Cs_7O_2 can be isolated. These formulæ are incompatible with the monovalence which is generally regarded as characteristic of the alkali metals.

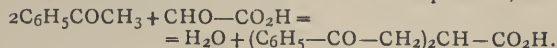
Vol. cxlviii., No. 19, May 10, 1909.

Influence of Radium on the Rate of Crystallisation.—Louis Frischauer.—When sulphur is allowed to crystallise, being meanwhile exposed to the action of radium, it is found that the number of centres of crystallisation is greatly increased, rising to double that in specimens of sulphur which were treated in exactly the same way but were screened from the effect of the radium rays by means of lead-foil. Moreover, the propagation of the crystallisation from drop to drop is more rapid. When crystallising sulphur is exposed to radium emanation it is found that the acceleration is caused by the induced activity rather than by the α -rays of the emanation. Probably the γ -rays of radium have no action upon the crystalline transformation, the effects being due only to the β -rays.

Anhydrous Compounds of Thorium Chloride with Alkaline Chlorides.—Ed. Chauvenet.—By direct fusion anhydrous thorium chloride can be made to combine with the alkaline chlorides, giving compounds of formula $\text{ThCl}_4 \cdot 2\text{MCl}$, where M is Li, Na, K, Rb, or Cs, and $\text{ThCl}_4 \cdot 4\text{MCl}$ with Rb and Cs only. Ammonium chloride

yields $\text{ThCl}_4 \cdot \text{NH}_4\text{Cl}$. This last compound is obtained by dehydrating the compound $\text{ThCl}_4 \cdot 2\text{NH}_4\text{Cl} \cdot 10\text{H}_2\text{O}$ at 150° .

Benzoylacrylic Acid. Condensation of Glyoxalic Acid with some Ketones.—J. Bougault.—Benzoylacrylic acid with potash or soda in the cold gives diphenylacetic acid, $(\text{C}_6\text{H}_5-\text{CO}-\text{CH}_2)_2\text{CH}-\text{CO}_2\text{H}$, the yield being greatly increased by the addition of acetophenone. This may be explained in two ways:—(1) Either one part of the benzoylacrylic acid condenses to give acetophenone and glyoxalic acid, and the acetophenone then reacts with the undecomposed benzoylacrylic acid; (2) or the acid entirely condenses to give acetophenone and glyoxalic acid, and the latter condenses with the acetophenone,—



From the fact that glyoxalic acid condenses very readily with acetophenone the second hypothesis seems most probably correct. The author has prepared by this method two new acids, dianisylacetic acid $(\text{CH}_3\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}_2)_2 \cdot \text{CH} \cdot \text{CO}_2\text{H}$, and dipiperacylacetic acid, $(\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CO} \cdot \text{CH}_2)_2 \cdot \text{CH} \cdot \text{CO}_2\text{H}$.

Modifications of Anthesterol and of its Benzoate.—T. Klobb.—By the action of reagents such as benzoyl chloride and different solvents upon anthesterol benzoate, different modifications can be prepared. Also anthesterol itself exists in different forms, and these are not stereoisomers, for their rotatory powers are all in the same direction. Some of the modifications may be due to polymorphism.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlii., No. 6, March 20, 1909.

Tautomerism of Aliphatic Ketones.—V. Hâncu.—Simple ketones of the aliphatic series can be converted into the enol form by the action of acetic acid anhydride and sodium acetate. Acetone is, however, an exception to the general rule, the result of the action being the condensation product mesityloxide. Mixed ketones of the same series do not behave like the simple ketones, but the author has not yet discovered the reason for this difference.

Organic Mercury Compounds.—Einar Biilmann and Johannes Witt.—Schrauth and Schoeller state that by the action of methyl malonic ester on mercuric oxide a mercury dimalonic methyl ester is obtained, and is converted into the anhydride of oxy-mercury acetic acid by saponification and the addition of acid. The authors, however, find that the compound obtained on repeating these experiments is a derivative of malonic acid and not of acetic acid, and appears to be derived from the mercury malonic acid described by Biilmann in 1902. They have observed that very slight alterations in the conditions of the experiment lead to unexpectedly great variations in the composition of the substances obtained.

Acetetyl Sulphide.—Emil Fischer.—On heating chloroacetal with an aqueous alcoholic solution of potassium sulphide or sulphhydrate to $120-150^{\circ}$, filtering, and evaporating the filtrate, a residue which gives an oily substance with water is obtained. After fractionation acetetyl sulphide may be separated from the product. Acetetyl sulphide, $\text{S} < \text{CH}_2 \cdot \text{CH}(\text{OC}_2\text{H}_5)_2$, is very readily dissolved by ordinary organic solvents. It gives an amorphous mass in liquid air. The smell of the pure liquid is faint and not characteristic, but when it is warmed with water it becomes considerably stronger and recalls other sulphides. It is rapidly dissolved by a 1 per cent solution of hydrochloric acid. The odour disappears, and a colourless liquid is obtained which gradually alters alkaline copper solutions on warming, and gives a silver mirror with ammoniacal silver solution.

Reductions with Sodium Amylate.—Otto Diels and Richard Rhodius.—A solution of sodium amylate is an energetic reducing agent, reducing benzaniline to benzylaniline, azobenzene to hydrazobenzene and isoamylaniline,

&c. It has for some time been known that sodium and amyl alcohol effect reductions which are not obtained with ethyl alcohol, and this difference has been ascribed to the higher temperature employed when amyl alcohol is used. This, however, is incorrect, for sodium ethylate does not reduce at the temperature of a boiling amylate solution.

Separation of Antimony and Tin.—G. Panajotow.—Antimony sulphide is completely soluble in strong hydrochloric acid on warming, and tin sulphide dissolves in dilute hydrochloric acid at the ordinary temperature. If acid of the right concentration is used the addition of sulphuretted hydrogen to the hydrochloric acid solution can be employed to separate the two metals. Antimony is precipitated quantitatively as sulphide at the ordinary temperature by a 15 per cent hydrochloric acid solution, while tin in acid of this concentration gives no precipitate with H_2S . In a mixture of the two metals after separation of the antimony trisulphide, the filtrate may be partially neutralised with ammonia, diluted with water, and then warmed and precipitated with H_2S . The precipitate of tin sulphide thus obtained can easily be filtered. This method of separating antimony and tin is very simple and rapid. It can be used in all cases in which antimony is in solution as trioxide, and it can also be applied for the separation of arsenic from antimony and tin by Nehr's method.

Determination of Tungsten.—M. Tschilikin.—Tungsten can be determined by means of α -naphthylamine, and the method gives good results. The compound formed has the formula $2(\text{C}_{10}\text{H}_9\text{N}) \cdot 5\text{WO}_3 \cdot 3\text{H}_2\text{O}$, and the reaction takes place at the ordinary temperature. From the results of analyses carried out by this method the author has found that commercial sodium tungstate has the formula $\text{Na}_2\text{WO}_4 + 2\text{aq}$.

Determination of Carbon in Aliphatic Compounds containing Hydroxyl in the Wet Way.—E. Berl and A. G. Innes.—A convenient method of determining carbon in aliphatic compounds is based upon the oxidation of the substance to CO_2 with chromic acid and phosphoric acid, the CO_2 being determined by Lunge and Rittener's method. Substances which are difficult to burn are often oxidised more easily if mercury is added. This method can only be applied to aliphatic derivatives; with aromatic compounds the result is too low, probably owing to the formation of CO and hydrocarbons which are not absorbed.

NOTES AND QUERIES.

. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Enamelled Iron.—I wish to ascertain whether the acid of milk affects detrimentally in any way enamelled iron vessels in which the milk may be deposited and allowed to remain for several hours from day to day.—B. Cook.

Estimation of Manganese.—(Reply to J. Williams).—Hugh Marshall (CHEMICAL NEWS, lxxxiii., 76, Feb. 15, 1901) discusses the (catalytic) function of the silver nitrate, and shows that "it seems to depend on formation and decomposition of silver peroxide."—CHARLES RATNER.

MEETINGS FOR THE WEEK

FRIDAY, 25th.—Physical, 5. "Transition-point in Zinc Amalgam," by Prof. Carhart. "Method of producing an Intense Cadmium Spectrum, with a proposal for the Use of Mercury and Cadmium as Standards in Refractometry," by T. M. Lowry. "Measurement of Wavelength for High-frequency Electrical Oscillations," by A. Campbell. "Electro-magnetic Method of Studying the Theory of and Solving Algebraical Equations of any Degree," by A. Russell and J. N. Alty. "The Sine Condition in relation to the Coma of Optical Systems," by S. D. Chalmers. Exhibition of a New Fery Thermo-electric Calorimeter, by C. V. Drysdale. "Instrument for Measuring the Strength of an Intense Horizontal Magnetic Field," by F. W. Jordan. "Method of Determining the Sensibility of a Balance," by Prof. Poynting and G. W. Todd. "The Balance as a Sensitive Barometer," by G. W. Todd.

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THE CHEMICAL NEWS.

VOL XCIX., No. 2587.

RADIUM EMANATION.

By A. DEBIERNE.

SOME months ago I began a series of experiments on the properties of radium emanation in a concentrated state. These experiments were rendered possible by the kindness of M^{me}. Curie, who placed at my disposal a solution containing a large proportion of radium (about 2 decigrms. of radium).

Ramsay, in collaboration with Soddy, Collie, and Cameron, has published several articles on the preparation and properties of radium emanation. The following are the most important results obtained by Ramsay and his collaborators. The emanation is a gas, and its volume can be determined; it possesses a spectrum of its own and gives rise to the formation of helium. Rutherford and Royds have confirmed these results by recent experiments; they have described the spectrum of the emanation very fully, and have given a photograph of it. They have also determined the volume occupied by the emanation in equilibrium with a given quantity of radium. However, the value they found, 0.6 cubic mm., for the emanation in equilibrium with 1 gm. of radium is very different from the latest value given by Ramsay and Cameron (7 cubic mm. for the same quantity of radium).

The observations made by me during this research on the whole confirm the above results. They agree particularly well with those of Rutherford and Royds.

The emanation set free by a solution of radium is mixed with a large quantity of hydrogen and oxygen produced by the decomposition of the water, with a smaller quantity of gases containing carbon and nitrogen produced by the decomposition of the grease of the stopcocks, and also with a little helium.

To eliminate the gases which can be absorbed (H, O, N, &c.) I employed the method which I used in 1905 to demonstrate the production of helium by actinium salts. By the action of copper and copper oxide the oxygen is absorbed, the hydrogen is transformed into water, and the gases containing carbon into CO₂; the water is absorbed by phosphoric anhydride and the CO₂ by fused potash; finally the nitrogen is absorbed by gently heated lithium.

The emanation is separated from helium by condensation by means of liquid air. A special apparatus is employed to obtain a fractional condensation and to observe separately the gases condensed at different temperatures and the uncondensed helium. The different gaseous portions are drawn by means of mercury into capillary tubes, the pressure is adjusted to that of the atmosphere, and the volume of gas is determined by measuring by a pair of dividers the length of the gaseous bubble and the diameter of the capillary tube. In some experiments each portion of gas was divided into two equal parts; one portion filled a little Plücker tube of some cubic millimetres capacity, and was used for the examination of the spectrum; the other part was compressed until atmospheric pressure was reached, and its volume was determined.

The portion of gas which is most strongly radio-active, and which consequently contains the greatest part of the emanation, is that which condenses between -175° and -150°. This gas gives a very brilliant characteristic spectrum. The first examination of the spectrographic plates shows no difference from those obtained by Rutherford and Royds. The spectrum of helium is absent at first; it appears gradually after a time, and in some cases becomes very bright.

The gas which cannot be condensed gives the spectrum of pure helium; I never detected the presence of neon in it.

The volume of the emanation diminishes fairly rapidly during the first hours following its preparation in the form of a bubble at atmospheric pressure. After this decrease, already observed by Ramsay and Soddy, the volume is fairly constant. Like Rutherford and Royds I have assumed that the volume measured after the initial contraction is the volume of the emanation.

The penetrating radiation emitted by the bubble of gas having been measured and compared with that emitted by a tube containing a known quantity of pure radium chloride, I could calculate the volume occupied by the emanation in equilibrium with 1 gm. of radium.

I have proved that for very different periods of accumulation of the emanation the volume obtained is always proportional to the activity. Thus for an accumulation lasting three days 0.6 cubic mm. of emanation are obtained for 1 gm. of radium; after six days, 0.52 cubic mm.; after nine days, 0.61 cubic mm.; after 32 days, 0.59 cubic mm. The mean value 0.58 agrees perfectly with the value given by Rutherford and Royds.

I have also determined the curves of the decay of the intensity of the radiation emitted by different portions of the gas. The condensable portions gave very concordant results; the half diminution is produced on an average in 3.81 days.

For the small quantity of emanation not condensed and mixed with helium the decay was a little slower (diminution to the half value in 4.1 days). Experiments to confirm this result and to study this anomaly are in progress.

(NOTE.—In an article which has recently appeared (*Phil. Mag.*, May, 1909) Rutherford reports on an analogous difference in the laws of decay. The simplest explanation of such a difference is to suppose that two distinct emanations exist, and that a fractionation of the two has been effected. Another explanation could also be put forward. The law of the destruction of the emanation shows that the different atoms have very different durations of life, the mean life only being constant. If no exterior cause intervenes to induce or influence radio-active transformations (which has not yet been proved) it must necessarily be supposed that the different atoms of the emanation at the moment when they are produced by radium are not all absolutely identical, since some of them are immediately destroyed, and others wait a very long time before being transformed. It can then be supposed that condensation has effected a certain selection between these different atoms).

During these experiments I noticed a curious phenomenon. Spontaneous electric discharges, visible in daylight, occurred in the little tubes containing the emanation at atmospheric pressure. These discharges are sometimes very frequent (some tubes would give a spark a minute). They often appear in the form of very fine sparks which may attain a length of some millimetres, and which are produced in the interior of the glass of the capillary tube. The tube is then furrowed with little cracks resulting from the passage of the sparks. These sparks very often start from a very brilliant point situated on the surface of the tube in contact with the emanation. Sometimes the electric discharge is produced across the emanation itself, which is fairly brightly illuminated. These disruptive discharges are only produced with certain kinds of glass. The glass which exhibited the phenomenon most often was a fusible glass which contained lead and which became violet under the action of the emanation.

Tubes made of glass containing a large proportion of lead did not exhibit the phenomenon of disruptive discharge.

This phenomenon may be attributed to the accumulation in the glass of the electric charges of the α - and β -rays emitted by the emanation when the glass is a sufficiently good insulator.—*Comptes Rendus*, cxlviii., 1264.

REACTIONS OF OXALATES.

By TARAK NATH DAS, B.Sc., Chemical Assistant of
Dr. Arthur Richardson, Ph.D.

THE method best adapted for the analysis of salts containing oxalates consists in evaporating the filtrate from Group II. to dryness and igniting the residue. This process is rather uneconomic of time and entails some care in managing the ignition. The following may therefore be generally substituted with advantage:—Dissolve the precipitate from $\text{NH}_4\text{Cl} + \text{NH}_4(\text{OH})$ in HNO_3 , add a little strong HNO_3 , and then some excess of KClO_3 . Boil vigorously for a few minutes; the oxalates will be completely converted into soluble nitrates, the C_2O_3 being completely oxidised to CO_2 and expelled.

Borates, fluorides, silicates, as can be seen, will be also partially removed along with the above by the action of HNO_3 .

The analysis is thus greatly facilitated, and can be completed in less than five minutes, even when all the complicated acid radicles are present.

Oxalic acid and alkaline oxalates can be also easily decomposed as above, although strong HNO_3 alone may be quite ineffective in some cases.

Tests for Oxalates.

When an oxalate is mixed with carbonate, sulphite, &c., the carbon monoxide evolved on treating with strong H_2SO_4 does not burn, unless the incombustible gases are first absorbed. The test can, however, be managed in a test-tube thus:—

Treat the mixture with dilute HNO_3 , and heat for some time till the evolved gases do not turn lime-water milky (separation from carbonates). Now add excess of KClO_3 and boil again; if the lime-water turns milky presence of oxalate may be inferred.

The quantitative study of the above along with analogous reaction is still proceeding.

Central Hindoo College,
Benares City, India.

SPACE RELATION OF FORCES IN THE ATOM.

By FRANK A. HEALY.

LET eight fields of force (electric charges, for instance) be arranged in space as at the eight corners of a cube. Let four of these be of one polarity and the other four of opposite sign. Four fields of like polarity are at the corners of a regular tetrahedron, similar to the arrangement of the valence bonds of the carbon atom. A sphere, within which the cube and the two tetrahedrons are inscribed, has the eight charges on its surface. The geometric figures are used simply to define the position and arrangement of the fields of force.

Since four of the fields of force are opposite in polarity to the other four, the algebraic sum of the field within the sphere is zero; the algebraic sum or effective value of the field outside the sphere is also zero. Now let the charge at one of the eight corners be doubled, let it be a negative charge. The total or effective value of the internal field is not zero now; designate its value as m . Now, in succession, let all four of the negative charges be doubled: the total internal field will have the values $m, 2m, 3m, 4m$. Next, let the four positive charges be successively doubled: the internal field will have the values $3m, 2m, m$, and 0, for in succession 1, 2, 3, and 4 pairs of fields become self-balanced or latent.

If now we begin to treble the charges in the same order we will again obtain the series of values $m, 2m, 3m, 4m$; $3m$ with one latent pair, $2m$ with two latent pairs, m with three latent pairs, and 0. The external field furnishes a series of the same sort each time. This succession of values will be repeated as often as we can add the unit charges.

This succession of values is identical with the normal succession of valence in the periodic table of the elements. Upon this fundamental regularity, of course, innumerable irregularities and complexities occur in the properties of the elements. The space relation of the valence of carbon and a few other elements had already been known, but by means of this we obtain the space relation of the valence bonds of every element of the periodic table except hydrogen.

The field of force may be electric or magnetic, or of some yet unknown manifestation of force possessing polarity.

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THE FRUIT OF *PYRUS ARBUTIFOLIA*.

By BURLEIGH B. REED.

THE fruit of *Pyrus arbutifolia*, commonly known as choke-berries, which was used in this investigation, was gathered in the vicinity of Sylvan Beach, New York, in August, 1907. The fruit consists of berries which were fully ripe when gathered. Their prevailing colour is dark purple to black, and they are globular in shape. When thoroughly dried they average 0.11 gm. in weight. There were 263 grms. on hand for this analysis. When burned the fruit gives off a heavy odour similar to burning straw. A sweet odour also develops which does not long remain. The fruit has a somewhat limited use as a food. It grows on shrubs 3 to 5 feet in height.

The Sugars.

In order to extract the sugars, 200 grms. of berries were placed in a litre flask, which was nearly filled with alcohol, and fitted with an inverted condenser. The alcohol was kept boiling on a hot water-bath for 150 hours. At first the alcoholic extract was removed twice daily, and fresh alcohol added. Later, the alcohol was changed but once each day. Each alcoholic extraction was of a beautiful cranberry-red colour, and gave a decided acid reaction with litmus. Finally the red colour of the extract changed to a brownish shade, and distilled water was substituted for the alcohol. The digestion was continued with successive portions of water for 160 hours until no more sugar was removed, as shown by Fehling's solution. The successive water extractions were placed in an evaporating dish, and evaporated down to a dark thick syrup. The syrup from the alcohol and water extractions were united, and aggregated 775 cc.

To determine the amount of sugar present, 0.05 cc. of the sugar was placed in an evaporating dish on the water-bath, and the alcohol removed by several additions of distilled water. The residue was dissolved in 50 cc. of water, removed to a beaker, and titrated while hot with standard Fehling's solution. This test showed 136.55 grms. or 68.27 per cent of sugar to be present in the berries. This checked fairly close with the 140 grms. loss in weight sustained by the fruit after the sugar had been extracted.

We added 50 cc. of the sugar solution to the same quantity of distilled water, and purified it by digesting with bone-black. The resulting solution was only a trifle coloured, and was used to determine the kinds of sugar. This purified solution was evaporated down as far as possible, when a thick sweet syrup resulted, slightly brown in colour, and tasting much like common corn-syrup. A number of tests were made, using 0.1 gm. of the sugar, 0.2 gm. of pure phenylhydrazine hydrochloride, 0.3 gm. sodium acetate in 2 cc. of distilled water. Each experiment showed one and three-fourths minutes as the time of osazone formation, pointing to fructose. The precipitates from these experiments were then united and crystallised from alcohol. The crystals were yellowish in colour, and melted at 204–205°, confirming the test for fructose. The cobalt nitrate test gave some indications of dextrose.

The Oils.

The residue from the sugar extraction was dried and weighed. There was found to be 60 grms. from which the oils were extracted. The residue was very finely ground, the fine powder was placed in a 500 cc. flask fitted with an inverted condenser. The flask was nearly filled with ether, and kept boiling on a warm water-bath for about 260 hours. At first fresh ether was supplied each day, but the changes were soon made less frequently. Each portion of ether, after its removal from the fruit, was distilled off, and the oil remaining was kept for later investigation. The oil was of a golden brown colour, and showed a faint tinge of green. The extraction was discontinued when about fifty hours of digestion secured only a small drop of oil. The total oil was purified by digesting in a small flask fitted with a condenser, with bone-black and ether. The solution was filtered, all traces of ether were removed, and the product was seen to be lighter in colour, and without the greenish tinge. The total oil obtained weighed 2.6849 grms. or 1.34 per cent of the original fruit.

As a check upon this result, the berries were dried and weighed after the oil had been extracted. They were found to have lost a little less than 1.50 per cent in weight. The specific gravity of the purified oil was found to be 0.80 at 15.5°. The oil did not solidify at a temperature of 18°, and no marked change was observed. The odour was similar to that of olive oil. Two saponifications were made, the amounts of oil used 1.0773 and 1.0308 grms. respectively. Each time twenty-four hours digestion on the water-bath was necessary completely to saponify the oil. The first portion was treated with alcohol and normal caustic soda solution, and titrated with normal hydrochloric acid, with phenolphthalein as the indicator. The saponification equivalent was found to be 637.4, thus indicating myricyl palmitate. The second portion was saponified, and the "Reichert number" of the oil obtained. The number obtained was 0.9, which signifies the number of cc. of tenth normal caustic soda required to neutralise the fatty acids. Allowing for probable hydrocarbon impurities which could not be removed on account of the small quantity of oil available, this test confirmed the palmitate result obtained by the first saponification. That a wax, hydrocarbon, or other foreign matter was present was shown when, after each saponification, an oily globule remained suspended in the flask. The very small amount of oil at hand made it impossible to separate out the fatty acids so as to obtain any satisfactory data concerning their character.

The Ash.

Five portions of berries averaging 2 grms. each were ashed in a platinum evaporating dish. The ash effervesces with hydrochloric acid.

I.	
Weight of berries ..	2.0097 grms.
Weight of ash ..	0.0432 "
SiO ₂ ..	Small trace
Fe ₂ O ₃ ..	2.54 per cent of ash
Al ₂ O ₃ ..	6.71 " "
CaO ..	16.20 " "
MgO ..	5.67 " "
II.	
Weight of berries ..	2.0707 grms.
Weight of ash ..	0.0911 "
SO ₃ ..	2.90 per cent of ash
III.	
Weight of berries ..	2.0722 grms.
Weight of ash ..	0.0847 "
P ₂ O ₅ ..	2.87 per cent of ash
IV.	
Weight of berries ..	2.0450 grms.
Weight of ash ..	0.0506 "
Na ₂ O ..	38.94 per cent of ash
K ₂ O ..	24.11 " "

The presence of these two substances was confirmed by the flame tests.

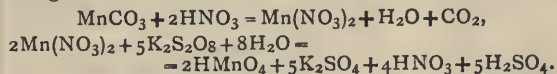
V.

This portion of the berries was ashed in order to make a quantitative determination of the small amount of manganese and chromium found to be present. The manganese was determined by dissolving the ash in 5 cc. of nitric acid, adding 0.5 of a saturated solution of silver nitrate, and the same quantity of a saturated solution of potassium persulphate, and diluting the whole with distilled water to a volume of 15 cc. The resulting pink colour was compared with a series of previously prepared potassium permanganate solutions of different strengths. By a comparison of colours, the amount of manganese was easily determined.

The chromium was determined in the same solution by adding 1 cc. of hydrogen peroxide. The resulting blue colour was compared with various strengths of a specially prepared solution of potassium bichromate. The following results were obtained:—

Weight of berries ..	4.0066 grms.
Weight of ash ..	0.0985 "
Mn ..	0.027 per cent of ash
Cr. ..	0.0012 " "

The equations that express the reactions for the manganese:—



The composition of perchromic acid, which is formed in connection with the estimation of chromium, is not understood.

Proteins.

The nitrogen was determined by the Kjeldahl method. We digested 1.0954 grms. of the berries for thirty hours with sulphuric acid. The nitrogen obtained was 0.84 per cent of the fruit. Several qualitative tests confirmed the existence of nitrogen.

The Acids.

Tests were made for a number of the more common organic acids, but only tartaric and citric acids were found.

I desire to record my gratitude to Dr. Knight for his many valuable suggestions during the progress of this work.

Cornell College, May 12, 1909.

A CONTRACT FOR RADIUM.

AN ascertained commercial value of £4 per milligram. (equivalent to £114,000 per ounce) has been placed upon radium by a contract just entered into between the British Metalliferous Mines (Limited) and Lord Iveagh and Sir Ernest Cassel for the supply of 7½ grms. (rather more than a quarter of an ounce) of pure radium bromide. This very large order for radium will be supplied from the above named company's mine near Grampound Road in Cornwall. In the short history of radium there has never hitherto been known any greater order than a gram. The first recorded order on a large scale will therefore be supplied from the British source from which several of the smaller orders have already been supplied. Messrs. Buchler and Co., of Brunswick, will produce the radium from the Cornish pitchblende under the superintendence of Prof. Giesel, their chief chemist. The 7½ grms. of radium referred to are to be presented by Lord Iveagh and Sir Ernest Cassel to the Radium Institute, for the formation of which they have already contributed very large funds. The Radium Institute, which will be under the surgical direction of Sir Frederick Treves, is expected to be ready to receive patients suffering from cancer about the end of the present year.—*The Times*, June 21, 1909.

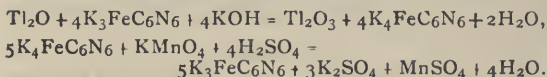
THE
VOLUMETRIC AND GRAVIMETRIC ESTIMATION
OF THALLIUM IN ALKALINE SOLUTION
BY MEANS OF POTASSIUM FERRICYANIDE.

By PHILIP E. BROWNING and HOWARD E. PALMER.

In a former paper from the Kent Chemical Laboratory of Yale University (Browning and Palmer, *Am. Journ. Sci.*, [4], xxvi., 83; *CHEMICAL NEWS*, xcvi., 106) it was shown that reactions involving oxidation by ferricyanide in alkaline solution and reoxidation by permanganate of the resulting ferrocyanide in acid solution might be applied to the determination of cerium in the presence of the other rare earth compounds.

In the work to be described the same reactions were applied to the volumetric estimation of thallium. A solution of thallium nitrate was made up by dissolving 10 grms. of pure thallos nitrate in water and making up to a litre. This solution was standardised by precipitating definite portions with potassium bichromate in alkaline solution, filtering, and weighing the thallos chromate (*Am. Journ. Sci.*, [4], viii., 460), and also by evaporating measured portions of the solution with an excess of sulphuric acid and weighing as the neutral sulphate (*Am. Journ. Sci.*, [4], ix., 137), the mean of closely agreeing results by both methods was taken as the standard.

Volumetric.—The procedure was as follows:—Measured portions of the solution of thallos nitrate were drawn from a burette, water was added to about 100 cc., a sufficient quantity of a solution of potassium ferricyanide to give an excess, and potassium hydroxide to complete precipitation of the brown thallic hydroxide. The precipitate was filtered off on asbestos, generally without settling, and washed thoroughly. The filtrate was acidified with sulphuric acid and titrated with standard permanganate. From the following equations, representing the reactions, the amount of thallium present may be readily calculated:—



It was found necessary to apply a correction for the amount of permanganate used to give the first tinge of pink colour to the amounts of ferricyanide used in the determinations. This seldom exceeded 0.1 of 1 cc. of the permanganate.

Table I. shows the results obtained with different amounts of the thallium salt.

TABLE I.

	Ti ₂ O taken as the nitrate.		Error.
	Grm.	Grm.	
1.	0.0809	0.0809	—
2.	0.0809	0.0808	-0.0001
3.	0.0809	0.0809	—
4.	0.1213	0.1212	-0.0001
5.	0.1213	0.1216	+0.0003
6.	0.1213	0.1218	+0.0005
7.	0.1213	0.1218	+0.0005
8.	0.1213	0.1212	-0.0001
9.	0.1213	0.1207	-0.0006
10.	0.1618	0.1614	-0.0004
11.	0.1618	0.1613	-0.0005
12.	0.1618	0.1616	-0.0002

Gravimetric.—The satisfactory character of the precipitate of thallic hydroxide obtained by this process suggested the possibility of applying it to a gravimetric estimation of thallium. Several precipitations were made according to the method described, and the precipitate contained in a perf rated platinum crucible upon an asbestos felt was dried over a low flame at about 200° C. to constant weight. The results are given in Table II.

TABLE II.

	Ti ₂ O ₃ taken as the nitrate.		Error.
	Grm.	Grm.	
1.	0.1305	0.1309	+0.0004
2.	0.1305	0.1314	+0.0009
3.	0.1305	0.1308	+0.0003
4.	0.0870	0.0872	+0.0002
5.	0.1740	0.1741	+0.0001
6.	0.1740	0.1739	-0.0001
7.	0.1740	0.1742	+0.0002
8.	0.1305	0.1307	+0.0002
9.	0.1305	0.1309	+0.0004
10.	0.1305	0.1308	+0.0003
11.	0.0870	0.0872	+0.0002
12.	0.0870	0.0874	+0.0004

In experiments 5 to 12 the precipitated thallic hydroxide was washed with hot water, a procedure to be recommended when large amounts are present. — *American Journal of Science*, xxvii., 379.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, June 10th, 1909.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

THE Croonian Lecture on "The Functions of the Pituitary Body" was delivered by Prof. E. A. SCHAFER, F.R.S.

"A Wave-length Comparator for Standards of Length." By Dr. A. E. H. TUTTON, F.R.S.

Two and a-half years ago the author was requested by the Standards Department of the Board of Trade to devise and superintend the construction of a new comparator, for comparing standards of length—the Imperial Standard Yard, for instance, with official copies, and the latter with the copies constructed for Local Authorities—in terms of wave-lengths of light. The instrument now described is the result. Besides performing its functions as a wave-length comparator, and being the first instrument specifically constructed as such, it is also the most perfect instrument yet devised for measurement in wave-lengths in general. It is described to the Royal Society by permission of the President of the Board of Trade.

The principle of the instrument is that of the author's interferometer, described to the Society in 1898 in connection with an interference dilatometer, and again as improved in 1904 in connection with the author's elasmometer or interference elasticity apparatus. The interferometer, which is totally different from that of Michelson or that of Fabry and Perot, is adapted as regards details in a special manner for the specific object in view, but with the exception that a Hilger constant deviation prism is employed instead of a train of two spectroscopic prisms, its principle is preserved intact.

The essential point of the instrument is that one of the two microscopes, employed to focus the two defining lines on a standard yard bar, actually carries just above the objective one of the two glass plates of the interference apparatus, which reflect the monochromatic light (hydrogen or cadmium red radiation) which is caused to interfere and produce rectilinear dark bands. When the microscope is moved the plate consequently moves with it, and the amount of movement is absolutely afforded by the movement of the interference bands, being equal to half the wave-length of the light employed for every band which passes the reference spot in the centre of the field of the interferometer telescope. So perfectly has this fine movement been achieved that the microscope and the bands can be caused to move simultaneously, by rotation of a large fine-adjustment wheel, so steadily that each band can be

made to pass the reference spot as slowly as one wishes, and be arrested instantly, without the slightest tremor, at any fraction of its width, so that the control of the bands and the counting is a perfectly simple matter.

In order to compare two standard bars, it is only necessary (1) to place the bar of known length, supported on an elaborate mechanism for the adjustment of the bars, also novel, under the two microscopes, carried on massive yet delicately-moving sliders on a 6-foot V-and-plane bed, so that the two defining lines are adjusted between the spider-lines of the micrometer eye-piece in each case; (2) to replace the standard by the copy to be tested, so that the defining line near one end is similarly adjusted under the corresponding microscope; then, if the other defining mark is not also automatically adjusted under the second microscope which carries the glass interference plate, as it should be if it is an exact copy; (3) to traverse that microscope until it is so adjusted; and (4) to observe and count the number of interference bands which move past the interference spot during the process. The difference between the bars is this number multiplied by the half-wave length of the light in which the bands are produced.

The paper also gives an account of the electrical and thermal arrangements as well as of the foundation masonry of the new comparator room. The temperature of the whole room is controlled entirely electrically, being maintained constant at the official temperature, 62° F. The thermostatic arrangements are of an original character, and of two different independent types—a thermometric and a resistance type.

"The Use of Wave-length Rulings as Defining Lines on Standards of Length." By Dr. A. E. H. TUTTON, F.R.S.

The delicacy of the method of measurement in wave-lengths described in the preceding communication calls for a corresponding refinement in the engraved lines which form the defining lines of the length of a standard yard or metre or other line-measure bar. The defining lines on the Imperial Standard Yard are sharp-edged, but contain the equivalent of forty interference bands of red light in their thickness, and the Benoit defining lines of the platinum-iridium copy made in 1902 are not only very ragged-edged, but contain fifteen interference bands in their thickness.

The author has been in communication with Mr. J. H. Grayson, of Melbourne, whose fine rulings have recently evoked such interest among microscopists, and after a long investigation has found that wonderfully satisfactory rulings on the scale of 40,000 to the inch can be made on polished speculum metal, covered with a thin cover-glass cemented only at the corners away from the rulings. Now the forty-thousandth of an inch is a single wave-length of red light (for $H\alpha = 1/38710$ inch and $Cd\ red = 1/39459$ inch), so that the interval between any adjacent pair of these lines is equivalent to only two interference bands. The thickness of each line, which is absolutely sharp-edged, is less than a single interference band. The author has therefore devised a defining mark in these rulings, which he terms a "Tutton location signal," to distinguish it from the "Benoit defining line." It consists of five such parallel lines spaced one forty-thousandth of an inch apart, with a pair of strong "finder" lines outside them and parallel to them, and another pair of similar finder lines perpendicularly transverse to them, to indicate a central part of the lines for use. The central line of the five fine Grayson rulings is the defining line.

These location signals can also be ruled on platinum-iridium, and with less success on gold and invar. But the result on speculum metal is so very superior that a large number of location signals have been made on this metal by Mr. Grayson for the Standards Department. The paper indicates their possible mode of use, not only as the end-mark defining lines of standard bars, but for a new mode of determining, by a stepping-off process of repeated doublings, the total number of wave-lengths of red cadmium light contained in the British yard.

CHEMICAL SOCIETY.

Ordinary Meeting, June 3rd, 1909.

Prof. HAROLD B. DIXON, F.R.S., President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Hardee Chambliss, Ph.D., 56, W. 36th Street, New York City, U.S.A.; Edward Walter Taplin, Church House, Meavittree, Exeter.

A certificate has been authorised by the Council for presentation to ballot under By-law I., Par. 3, in favour of Dr. Hassam A. Lakhani, Murud Janjira, India.

Prof. FRANK WIGGLESWORTH CLARKE, of Washington, then delivered the Wolcott Gibbs Memorial Lecture, at the conclusion of which Prof. Sir JAMES DEWAR moved a vote of thanks to Prof. Clarke.

Prof. THORPE, in seconding the motion, congratulated the Society in securing in their Honorary Foreign Member, Prof. Clarke, one so eminently capable of doing justice to the signal services which his deceased countryman, the late Dr. Wolcott Gibbs, had rendered to chemical science. The Chemical Society justly prided itself on the distinction conferred upon it by the distinguished men who constituted the class of its Honorary Members. They honoured them living, and when death summoned them from the scene of their activities they sought to honour them dead, and by lectures such as they had heard to-night to commemorate their achievements and to indicate their relation and true position towards the science which they had laboured to advance. In putting together the story of Dr. Wolcott Gibbs's life and work, Dr. Clarke had enjoyed the advantage of contact and intimate personal acquaintance with his subject, and it was this personal note which rendered his discourse specially interesting and valuable.

Prof. OTTO N. WITT expressed his great satisfaction at having been able to listen to Professor Clarke's lecture, which not only deserved the greatest praise for its literary and scientific merits, but had also a great personal interest for himself.

In the German Chemical Society it was customary for the death of prominent members to be announced by the President in the meeting following the sad event, and a short biographical sketch had to be given on such occasions, pending the publication of an elaborate essay at the end of the year. Thus it had been his (the speaker's) duty to give an account of the life and labours of Wolcott Gibbs in one of the meetings of the Society. In compiling the necessary notes, he had observed how scant the existing information was, and the short time at his disposal had not allowed him to ask Professor Clarke for a few notes as he would like to have done. There were a few things, however, which made it quite certain that Gibbs, who was an Honorary Member of the German Chemical Society as well as of the English one, had been deserving of the greatest esteem. It was quite evident that he had enjoyed the sincere friendship of the great founder of the German Society, A. W. Hofmann, whose name was also a household word amongst English chemists. And it was equally certain that Gibbs possessed great merits as a teacher and as the head of the brilliant and successful school of American chemists, of which Professor Clarke, whom the speaker had learned to know and to admire during his stay in the United States, was the most distinguished representative. Whilst supporting the motion for a vote of thanks to Professor Clarke, he begged to thank the President for having given him this opportunity for paying a tribute of personal admiration both to the memory of Wolcott Gibbs and to Professor Clarke, who had pictured the life and the work of his dead master in words that had come from the depth of his heart.

Prof. CHARLES BASKERVILLE said that the honour paid him by the President in asking him to support the vote of thanks proposed by Sir James Dewar was, he knew, intended as a personal one. He was endeavouring to fill the Chair, the third in line, first occupied by the distinguished lamented subject of Dr. Clarke's eloquent

eulogy. He wished, however, to emphasise something more significant. As mentioned by the lecturer, Wolcott Gibbs was the founder of the Union League Club of New York, which organisation sought to preserve the Union. His (the speaker's) father and all his relations sought to dismember that Union for reasons they thought good. The Union was happily preserved, however, and a scion of the Confederate States was now carrying forward the educational work inaugurated by the deceased patriot. Chemistry thus showed itself in a social way as the crucible of civilisation.

It gave him peculiar personal pleasure to support the motion for another reason unknown to many of those present. Professor Clarke was his chemical grandfather, for he taught Professor Dudley, who was also present, and who in turn had taught him (the speaker). His pride in the delightfully charming manner in which Dr. Clarke, the pupil, had shown his appreciation of his former master could therefore well be understood.

The PRESIDENT said that, in its Memorial Lectures, he thought the Chemical Society had learnt to look for three excellences.

They wished in the first place to have recorded the main steps in the career of the distinguished chemist whom they were met to commemorate, so that they might appreciate the difficulties he faced and how he surmounted them—difficulties which could only be made real to them by one who was a past master of their science; secondly, they looked for some personal and sympathetic touches to tell a younger generation what kind of man was he who was gone; and lastly, they were delighted when the story was told them, not only scientifically and sympathetically—but with that arrangement and perspective and charm of language which could turn even chemistry into literature.

They could congratulate themselves that in all these excellences the lecture of Professor Clarke fulfilled, and more than fulfilled, their ideals.

The vote of thanks was put to the meeting, carried by acclamation, and acknowledged by Prof. CLARKE.

Of the following papers, those marked * were read:—

*154. "*The Molecular Weight of Tetraethylammonium Bromide and the Atomic Weight of Carbon.*" By ALEXANDER SCOTT.

The author gave an account of his endeavours to determine the molecular weight of a hydrocarbon with a degree of accuracy comparable to that attained in the determination of the atomic weights of many elements. This has been done for C_8H_{16} by titrating pure tetraethylammonium bromide against pure silver, after the manner of Stas. To precipitate 107.93 parts of silver, 210.324 parts of $N(C_2H_5)_4Br$ were required, whilst for the same weight of silver 97.995 parts of ammonium bromide were necessary. Subtracting from—

$$\begin{array}{r} 210.324 = N C_8 H_{20} Br \\ 97.995 = N \quad H_4 \quad Br. \\ \hline \end{array}$$

we obtain—

$$112.329 = C_8 H_{16}$$

If we take $H = 1.0075$, then $H_{16} = 16.12$, which gives $112.329 - 16.120 = 96.209 = C_8$ or $C = 12.026$.

This number has been corroborated by a titration made in the same way of a small quantity of tetramethylammonium bromide, which gave $154.150 = N(CH_3)_4Br$, and, similarly, 56.155 for C_4H_8 and $C = 12.024$. Taking 107.88 as the atomic weight of silver, we get $C = 12.018$.

DISCUSSION.

Prof. F. W. CLARKE called attention to the fact that the new value proposed for the atomic weight of carbon was notably higher than that found by recent investigators with physical methods. From the densities of carbon dioxide, carbon monoxide, and methane, the atomic weight of carbon was very near 12. In Lenher's determinations of the atomic weight of tellurium, a value had just been found of 127.33, calculated with the international figures for silver, potassium, chlorine, and bromine of several years ago.

This result was lower than the best results obtained by others. But on re-calculating Lenher's work with the new value for the other atomic weights, the value for tellurium was 127.55, in close agreement with former determinations. Hence, the discrepancy was due, not to the work done, but to the antecedent factors used in calculation. How far the discordance in the figures for carbon might be due to similar causes it was too soon to say, but part of it was thus to be explained.

Sir W. RAMSAY called attention to the possibility of included mother-liquor in the ammonium bromide and the tetraethylammonium bromide.

In reply, Dr. SCOTT pointed out that the methods employed in precipitating and drying the various specimens of the salt, as well as the very close agreement of the results, seemed to exclude all probability of the dried salt containing any mother-liquor. The atomic weight taken for silver (107.93) rendered the results more readily comparable with those of Stas, whilst the value 107.88 at present adopted by the International Committee, as Dr. Thorpe had pointed out, was probably only of transient interest, and might, by further research, be still further lowered.

155. "*The Rate of Formation of Azo-derivatives from Benzenoid Diamines.*" By VICTOR HERBERT VELEY.

It was shown that (i.) the rate of formation, as studied by a tintometer method of azo-compounds from benzenoid diamine hydrochlorides and sodium nitrite is conditioned by the hydrochloric acid and monohydrochloride liberated by hydrolysis. It is an example of a simultaneous linear reaction expressed simply as $\Delta x / \Delta t = k$.

(ii.) The total amount of dye-stuff capable of being formed, or range, is a linear function of concentration, but the increase of rate is a logarithmic function of the concentration expressed as $\log k_n = \log k_1 + a \log c$ (c = concentration, a = constant to be evaluated from the results).

(iii.) The rate is a logarithmic function of absolute temperature according to the expression $k_1/k = (T_1/T)^m$.

(iv.) The addition of hydrochloric and other acids produces an initial acceleration, but a total retardation, the reaction sooner coming to an end, and consequently the amount of dye-stuff capable of being formed is thereby diminished.

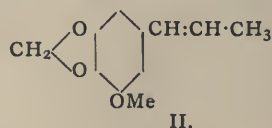
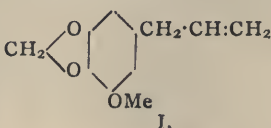
(v.) The substitution of hydrogen by the methyl grouping (comparison of phenylene- and tolylene-diamine—Bismarck Brown and Vesuvine) causes a slight decrease in rate, but a considerable decrease in the total amount of dye-stuff capable of being formed.

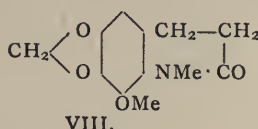
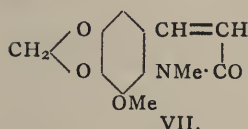
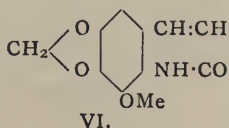
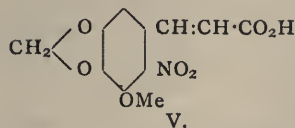
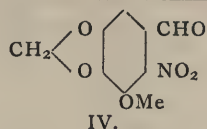
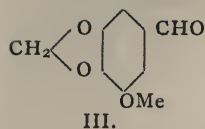
It is considered probable that this is a result of the more ready decomposition of the intermediate diazo-compound in the case of the latter than in that of the former.

156. "*The Synthesis of Substances Allied to Cotarnine.*" By ARTHUR HENRY SALWAY.

The material employed as the starting-point in this investigation was myristicin (3-methoxy-4:5-methylenedioxy-1-allylbenzene), which was obtained from the essential oil of nutmeg (compare Power and Salway, *Trans.*, 1907, xci., 2037). The successive stages in the synthesis are represented by the following compounds:—I., myristicin; II., isomyristicin; III., myristicinaldehyde; IV., nitromyristicinaldehyde; V., nitromethoxymethylenedioxybenzoic acid; VI., ketomethoxymethylenedioxydihydroquinoline; VII., ketomethoxymethylenedioxydihydroquinoline; and VIII., oxyisocotarnine.

Ketomethoxymethylenedioxydihydroquinoline, keto-methoxymethylenedioxydihydroquinoline, and oxyisocotarnine are closely related to cotarnine, and their physiological action is at present under investigation.



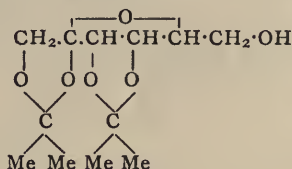


An account was also given of several attempts to synthesise cotarnine, which, however, were unsuccessful.

157. "Monomethyl Lævulose and its Derivatives. Constitution of Lævulosediacetone." By JAMES COLQUHOUN IRVINE and ALEXANDER HYND.

Lævulosediacetone yields on methylation by the silver oxide reaction a crystalline derivative (monomethyl α -lævulosediacetone), melting at 115° , and having $[\alpha]_D^{20} -136.4^\circ$ in methyl-alcoholic solution. The compound is very easily hydrolysed by dilute acids to give monomethyl lævulose, which is apparently the first definite example of a mono-substituted sugar other than the glucosides or the metallic derivatives. The sugar crystallises from ethyl acetate in the pure α -form, which displays mutarotation in the downward sense:— $[\alpha]_D^{20} -70.5^\circ \Rightarrow -53.1^\circ$. On the other hand, fusion gives an excess of the β -form, and the reverse optical change ensues on solution. The compound yielded monomethylglucosazone as yellow needles, melting at 142° , and was oxidised by bromine water to α -8-dihydroxy- γ -methoxybutyric acid.

These results show that the methyl group in the alkylated ketose is in the δ -position with reference to the reducing group, and according to this view, the structure of lævulosediacetone must be—



In addition, it has been shown that the alkylated sugar condenses readily with acetone or with methyl alcohol, and the products thus obtained are interconvertible under suitable conditions. The specific rotations of the various compounds described show that the total optical effect resulting from complete methylation of the sugar molecule is the additive sum of oppositely directed values.

158. "Optically Active 4-Oximinocyclohexanecarboxylic Acid and the Configuration of the Oximino-group." (Preliminary Note). By WILLIAM HOBSON MILLS and ALICE MARY BAIN.

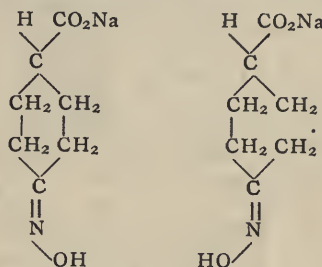
When a sufficiently dilute solution of equimolecular proportions of 4-oximinocyclohexanecarboxylic acid (W. H. Perkin, *Trans.*, 1904, lxxxv., 427) (4.7 grms.) and quinine (9.7 grms.) in ethyl acetate is allowed to evaporate slowly at the ordinary temperature, a quinine salt crystallises in silky needles during the course of two or three days.

The salt thus obtained was re-crystallised three times from ethyl acetate and then decomposed by suspending it in water, carefully adding a slight excess of dilute aqueous sodium hydroxide, and extracting repeatedly with ether to

remove quinine. There was thus obtained a slightly alkaline solution of sodium salt, from which all quinine had been removed, corresponding with about 1.8 grms. of oximino-acid. On polarimetric examination in a 2 dcm. tube, very distinct lævorotation was observed, namely, $\alpha_D -4.4^\circ$. The optical activity was immediately destroyed by acidification with dilute hydrochloric acid.

From the above observations, it appears probable that the sodium salt of 4-oximinocyclohexanecarboxylic acid can exist in a dextro- and lævo-modification, as well as the inactive form corresponding with the acid described by Perkin.

Since in a compound of this constitution enantiomorphism is possible only if the three valencies of the nitrogen atom of the oximino-group do not lie in one plane, the two active forms must correspond with the two configurations,—



(NOTE.—An alternative constitution for the active salt, $\text{CO}_2\text{Na}\cdot\text{CH}\langle\begin{smallmatrix}\text{CH}_2\text{CH}_2\\\text{CH}_2\text{CH}\end{smallmatrix}\rangle\geq\text{C}\cdot\text{NH}\cdot\text{OH}$, is very improbable, since acidification, which would be expected to favour the grouping $\text{:C}\cdot\text{NH}\cdot\text{OH}$ relatively to C:NOH , at once destroys the activity).

The existence of an optically active form of this substance thus affords evidence of the validity of the fundamental hypothesis in the Hantzsch-Werner theory of the isomerism of the oximes. It is also of interest in connection with the recent work on optically active substances which do not contain an asymmetric carbon atom in the narrower sense (Perkin and Pope, *Trans.*, 1908, xciii., 1075; Harding, Howth, and Perkin, *Trans.*, p. 1943; Perkin, Pope, and Wallach, *Proc.*, 1909, xxvi., 83; also Marckwald and Meth, *Ber.*, 1906, xxxix., 1171, &c.).

The authors are proceeding with this investigation, and hope in due course to submit a complete account of their results.

159. "Cyclobutane-1:3-dicarboxylic Acid and some of its Derivatives." By WILLIAM HENRY PERKIN, jun., and JOHN LIONEL SIMONSEN.

The authors described the action of hydrobromic acid and of bromine on cyclobutane-1:3-dicarboxylic acid, and on norpinic acid, and discussed the conditions under which disruption of the cyclobutane ring takes place in these and analogous cases.

160. "The Oxidation of Mucic Acid in presence of Iron." By FREDERIC FERRABOSCHI.

The oxidation of mucic acid by means of hydrogen dioxide in presence of iron has been investigated. The principal product is a strongly reducing acid, which appears to be a dihydroxymucic acid. It may also be regarded as a diketonic acid, namely, dihydroxydiketoadipic acid. Its dihydradzone has been prepared.

Parallel experiments on the oxidation of saccharic acid gave analogous results, but the products obtained are not identical with those derived from mucic acid.

161. "The Production of Ozone in the Interaction between Hydrogen Dioxide and Sulphur Dioxide." (Preliminary Note). By FREDERIC FERRABOSCHI.

In an investigation of the well-known reaction between sulphur dioxide and hydrogen dioxide, it has been observed that ozone is produced in considerable quantities.

It is found that when sulphur dioxide is rapidly led into

a solution of hydrogen dioxide (both "10 volume" and "20 volume" strengths were used), it is entirely destroyed in passing through a layer 2 or 3 cm. deep. Each bubble almost, but not entirely, disappears, and ozone is produced in quantities sufficient to be easily detected by its odour. Its presence may be further proved by its actions on starch-potassium-iodide paper, and on paper moistened with an acetic acid solution of *pp'*-tetramethyldianinodiphenylmethane ("tetra-base").

The production of ozone can also be observed when excess of hydrogen dioxide is added to aqueous sulphurous acid.

The same effect is not produced in the reaction of hydrogen dioxide with sodium sulphite or thiosulphate, or when sodium or barium peroxides, either with or without an acid, are added to aqueous sulphurous acid.

The reaction is being examined quantitatively.

162. "*The Action of Sulphur Monochloride on Salts of Organic Acids; a Convenient Method of Preparing Anhydrides.*" By WILLIAM SMITH DENHAM.

When sodium benzoate is boiled with a solution of sulphur monochloride in light petroleum, a compound of the probable formula $(C_6H_5 \cdot CO_2S)_2$ is formed, which is very unstable and soon decomposes, giving sulphur, sulphur dioxide, and benzoic anhydride. The formation of this compound takes place more easily if the silver salt is used. Similar derivatives of acetic, propionic, phenylacetic, and the toluic acids have been obtained.

The easy formation and simple decomposition of these compounds suggests a method of preparing the anhydrides of the acids.

Similar monochloride reacts also with metallic derivatives of imides.

163. "*The Velocity of Decomposition of Nitroglycerin by Heat.*" (Part I.). By ROBERT ROBERTSON.

Nitroglycerin (glyceryl trinitrate) is heated in a current of carbon dioxide in an apparatus arranged to condense any volatilised nitroglycerin, and, on rotation about an oblique axis, return it to be again heated. The nitrogen peroxide evolved is determined by Robertson and Napper's spectroscopic method (*Trans.*, 1907, xci., 761). The products of decomposition are then passed over red-hot copper and copper oxide, and the nitrogen is measured over potassium hydroxide. It was found that nitroglycerin decomposes uniformly, yielding nitrogen peroxide, that the rate of decomposition is a function of the temperature, being doubled for every 5° between 95° and 125°, and that the rate of decomposition is higher than that of gun-cotton.

PHYSICAL SOCIETY.

Ordinary Meeting, June 11th, 1909.

Dr. C. CHREE, F.R.S., President, in the Chair.

A PAPER by Dr. RUSSELL and Mr. ARTHUR WRIGHT on "*The Arthur Wright Electrical Device for Evaluating Formulae and Solving Equations.*" was read by Dr. Russell.

In this device special slide resistances are used. If R be the resistance of one of these and a metallic finger make contact with it at a point where the scale-reading is x , the resistance between this finger and the terminal of the slide is R/x . The scales of the slides are graduated logarithmically as in the ordinary slide-rule. Hence the processes of multiplication and division can be done mechanically by sliding them against exactly similar fixed scales. If we connect a number of these slide resistances in parallel, since the current is inversely proportional to the resistance, the sum of the currents through them will be proportional to the sum of the readings of the contact fingers. We can easily balance by a null method this current against the current going through a single slide resistance X by means of a Wheatstone's bridge arrangement. In this case the reading on X when there is a

balance gives the sum of the readings on all the other slides. Similarly we can subtract numbers by putting slides representing these numbers in parallel with X and then obtain a balance by altering the reading on X . It is also shown how the variable arms of the bridge can be usefully employed in making the calculations.

By clamping the contact fingers inclined at certain angles to a rod which can be moved at right angles to the slides, it is easy to obtain the values on X of $f(x)$ when—

$$f(x) = ax^m + bx^n + cx^p + \dots,$$

where the indices $m, n, p, \dots$ may be positive, negative, or fractional, and the coefficients may be positive or negative numbers. In particular if the reading on X be zero when x is x_1 then x_1 is a root of the equation $f(x) = 0$.

A model of this device for solving an equation of any degree consisting of not more than four terms was shown. In this model the slide resistances are fixed on a rigid framework and the contact fingers are wires which can be fixed at any desired angles $\cot^{-1} m, \cot^{-1} n$, and $\cot^{-1} p$ with the slides, where m, n , and p are the indices of the powers of x in the equation. A few dry cells and a lecture-table galvanometer were employed. Moving the framework until there is no deflection of the galvanometer, the pointer attached to it indicates at once a root of the equation. The inaccuracy of the results found by means of this model is of the order of one per cent. It is explained how approximate values of the imaginary roots of numerical equations can be found by the device. It is also explained how it can be employed to solve very complicated equations. It is shown, for instance, that a device with four slide resistances like the model exhibited can be used to find approximate values of the roots of numerical equations of the form—

$$a/x^m + b/f(x) = cx^n + dF(x),$$

when the values of $f(x)$ and $F(x)$ have been computed or found experimentally for various values of x . The same device also can be used to find approximate values of x which satisfy the equation—

$$a_1 l_1 b_1 x + a_2 l_2 b_2 x + a_3 l_3 b_3 x + a_4 l_4 b_4 x = 0$$

when the numerical values of the constants are known.

Prof. C. H. LEES expressed his interest in the device and referred to the large number of calculations that could be performed with it.

Dr. W. H. ECCLES congratulated the authors, and referring to the fact that the machine could be used to solve a bi-quadratic, asked if it was possible to determine the two quadratic factors by means of it.

A paper on "*The Echelon Spectroscope, its Secondary Action and the Structure of the Green Mercury Line*" was read by Mr. H. STANSFIELD.

The paper describes an investigation of the action of an echelon spectroscope and the results obtained as to the structure of the green mercury line given by an Arons lamp. The echelon spectroscope employed was arranged so that the auxiliary prism could be mounted next to the echelon. The dispersion of the prism may be added to, or subtracted from, the dispersion of the echelon, and the change of 4 per cent in the dispersion thereby obtained gives a method of determining whether two lines in the spectrum belong to the same order. The theory of the primary action of the echelon in the reversed position, when the light leaves by the largest plate, is compared with the theory of the echelon in the usual position. Fabry and Perot spectra are produced by the secondary action of the echelon, that is by the reflection of light at the surfaces of the plates. When the echelon is tilted the twice reflected or secondary light may be separated from the primary and parts of the Fabry and Perot circles observed with a wide slit. The secondary light also undergoes the primary echelon treatment, and, with a narrow slit, is confined to the points of intersection of the two systems of spectra, giving spectra similar to those obtained by Gehrcke and Baeyer by crossing two plane-parallel

plates, a single wave-length being represented by a point in each order and a short continuous spectrum by a line. When the echelon is in the ordinary position, the secondary spectra are lines similar to the primary echelon lines and may be observed moving across the broad central line when the echelon table is slowly rotated; they show up much more clearly on the continuous background of the spectrum of the green line given by a hot quartz lamp. The results as to the structure of the green line are compared with other echelon results and with those published by Gehrcke and Baeyer. The agreement between the independent methods, as to the number and position of the components, is now fairly close.

Dr. LEES referred to the importance of the secondary action, and asked the author if it was now possible to say definitely whether a line observed in an echelon spectrum is genuine or is produced by the instrument.

THE AUTHOR said that Gehrcke and Baeyer had hoped to supply the means of settling doubts of this kind when they eliminated the ghosts from their green line spectrum by their method of "interference-points." Since then, however, two faint lines had been added to the list of components. With the possible exception of one faint line agreement had now been arrived at between two independent methods.

A paper entitled "*The Proposed International Unit of Candle Power*" was read by Mr. C. C. PATERSON.

The paper discusses the units of Candle Power at present officially accepted in Great Britain, France, the United States of America, and Germany. The numerous intercomparisons which have taken place during the past five years between these units show that the candle, as interpreted in France, Great Britain, and the United States respectively, has practically the same value in the three countries. The authorities in the gas and electric interest in the United States are prepared to adjust their units of candle power to bring them to a single value which is to be the same as the British and French units. The paper gives the results of comparisons showing that within the limits of experimental error the British and French units are identical. The change involved in the unit at present maintained at the Bureau of Standards, Washington, is shown to be 1.6 per cent. The agreement thus established forms the subject of an official memorandum from the National Physical Laboratory (with the concurrence of the Metropolitan Gas Referees), the Bureau of Standards, Washington, and the Laboratoire Centrale, Paris. The proposal to call the common unit of light to be maintained jointly by the National Standardising Laboratories of America, France, and Great Britain the "International Candle" has been submitted to the International Electro-technical Commission, and through it to all the countries of the world which are represented on that Commission. The Hefner unit is shown to be almost exactly 9.10ths of the new unit. The comparisons between the units have been made by two methods:—(1) The direct comparisons of the flame standards in France, Germany, and Great Britain. (2) Through the medium of electric sub-standards which have had values assigned to them in the National Laboratories of the four countries.

The agreement between the ratio values by the two methods is very close, and is shown by a table giving the results of the various comparisons which have been made.

Dr. FLEMING said that it was interesting to hear that the chief Powers had come to an understanding with each other as to the Unit of Light. It must be remembered, however, that this proposed International Unit had no objective existence, and no greater value as a suit of comparison than the Hefner or Pentane units, to which it was related by an arbitrary definition. Dr. Fleming said that he greatly regretted that the National Physical Laboratory authorities had acquiesced in the adoption of a flame standard of light with all its difficulties and variabilities. Influenced as they are by atmospheric pressure, moisture, CO₂, height of flame, composition of fuel, and number of

persons in the photometric room, these flame standards could not possibly be considered as a final solution of the problem of obtaining a primary standard of light. What was really required was the concrete realisation of a permanent primary standard, which would be the standard of reference for secondary standards like the Fleming Ediswan large-bulb glow-lamp standards, which he (Dr. Fleming) had introduced seven years ago. Dr. Fleming remarked that Mr. Paterson made only a very brief reference to M. Violle's work on the platinum standard, and ignored altogether the careful work of Professor Petavel carried out in 1899 in the Davy-Faraday Laboratory. Professor Petavel's conclusions were that with suitable precautions the unit of illumination could be reproduced within 1 per cent by means of the molten platinum standard. He asked Mr. Paterson if any attempt had been made at the National Physical Laboratory to repeat or extend Prof. Petavel's work, and if not why not? Investigations of this kind, which were difficult to carry beyond a certain point in private laboratories, were peculiarly the province of a State-aided institution like the National Physical Laboratory.

Dr. Fleming remarked that he was pleased to see that Mr. Paterson endorsed the conclusions which he (Dr. Fleming) had stated seven years previously in a paper read before the Institution of Electrical Engineers, viz., that properly prepared (large bulb) glow lamps constitute the best secondary standards. He (Dr. Fleming) had now employed for fourteen years secondary standards of this type, and had not found anything to surpass them in convenience and accuracy. The flame standards were unequally affected by changes in atmospheric pressure and moisture. Hence any figures for ratios such as are given in Mr. Paterson's paper are true only under certain accurately defined conditions of surrounding atmosphere which are very difficult to reproduce. Accordingly elaborate experiments to ascertain how many Hefners are equal to 1 Pentane is not a matter of nearly such importance as the construction of some final constant primary standard of light, and in his (Dr. Fleming's) opinion the most satisfactory form for this primary standard of light is to derive it from the light emitted normally by a defined area of some substance in a state of incandescence at a known fixed temperature. He was sure that many practical photometrists, especially those connected with the electric lighting industry, were not at all convinced that the best primary standard was a flame standard, or that the Pentane or Hefner units were a completely satisfactory solution of the problem of obtaining a primary standard of light.

Dr. RUSSELL complimented the author on his experimental results. The *bougie décimale* was the unit adopted by the International Congress of Electricians in 1889, and was defined to be the twentieth part of the Violle standard. He was not prepared to accept that it was equal to 1.11 Hefner unit. Lummer's and Petavel's results rather discounted the importance to be attached to Violle's number. In connection with Dr. Fleming's remarks he stated that the unit suggested by Waidner and Burgess had many advantages. They proposed to adopt as the unit of intensity the radiation from a square centimetre of a black body maintained at the temperature of the fusion of platinum. He referred also to the unit suggested by Steinmetz, and as Mr. Dyott was present he asked if he could give any information about this unit.

Mr. DYOTT said that his experiments had been made exclusively in connection with Professor Steinmetz's magnetic arc. He had made no experiments on his photometric unit.

Mr. DOW said the pentane lamp as a standard was not very inferior to the Violle standard. He did not think we could as yet accept as a standard an area of a black body at a high temperature.

Dr. DRYSDALE thought that Mr. Paterson was to be congratulated on his summary, and the International agreement arrived at was most welcome. As he understood the paper, however, it was simply an attempt to obtain agreement between present existing units rather than standards,

and left the matter of the best form of standard perfectly open. He thought that everyone having experience with flame standards would thoroughly agree with Professor Fleming's condemnation of them, and there could be no doubt that the primary standard should be an incandescence one. He, however, did not agree with Dr. Fleming's suggestion of reviving the Violle standard. What was wanted in an incandescence standard was a definite area of a definite surface at a definite temperature. When the Violle standard was suggested we had little knowledge of the radiating properties of surfaces, or high temperature measurement, and therefore the only suitable thing was to take a very pure substance, using its melting-point as a bench-mark of definite though unknown temperature. But everyone who had studied the history of the Violle standard was aware of the great difficulties of setting it up, and it had the disadvantage, according to Petavel, that the surface was dependent on the gas mixture used, besides an extremely short period of constancy and high expense. In the meantime we have realised that a perfectly black body is easily obtainable, and that it has perfectly definite radiating properties, we have the laws of Stefan and Wien, and optical pyrometry has advanced to a high degree of accuracy, and it therefore seemed decidedly preferable to suggest a unit area of a black body at a definite temperature. Mr. Jolley and he had come to the conclusion that a square cm. of a black body at a temperature of 2000° absolute would perhaps be a good unit, and would be probably of the order of 100 candle-power. This temperature was probably pretty close to that of the ordinary carbon filament glow-lamp, so that there should be no colour difficulty, and it should not be exceptionally difficult to maintain constant. If the temperature were measured by an optical pyrometer of, say, the Fery form based on the Stefan law, the deflection would be proportional to the 4th power of the absolute temperature, while the light according to Lummer and to integration from Wien's law was proportional to T^{12} . Hence the light would be proportional to the cube of the deflection only, and the probable error would not be large. Finally, a point in favour of the black body was the perfectly definite character of its spectrum, which made it a standard of colour as well as intensity, and suitable for spectrophotometric comparison. As the surface would be that of a solid, it would be unnecessary to maintain it in a horizontal position, as with the Violle standard, and the amount of light could be easily varied by a diaphragm.

Dr. Drysdale said that he thought Mr. Dow had slightly misunderstood the nature of Professor Fery's results, and it would be unfortunate if this should militate against the idea of the black body as a standard. There was no difficulty in obtaining a perfectly black body either by an enclosure or reflector. What Professor Fery's recent experiments had shown was not that Kurlbaum's black radiators were at fault, but that he had been in error in assuming the perfect absorption of platinum-black with which his receiving bolometer was coated. This had necessitated an increase of the constant in the Stefan formula from Kurlbaum's value of 5.32 to 6.32, but this was a point which could easily be settled, and did not indicate any real difficulty in the use of the black body or the determination of its temperature, which could be simply extrapolated from known temperatures by the aid of the Stefan law.

Prof. C. H. LEES said that Professor Petavel's recent work on the radiations from heated platinum strips suggested that he was not altogether satisfied with the Violle standard.

Mr. PATERSON expressed his interest in Dr. Fleming's remarks, and said he had probably misunderstood the object of the paper which dealt with the relations existing between the various units now in use. He agreed with his observations on the flame standard. He had not referred in his paper to the work of Dr. Fleming and Professor Petavel on the Violle standard as it hardly came within the scope of the paper. They had not tried to

reproduce the Violle standard at the National Physical Laboratory. With regard to Dr. Drysdale's remarks about the use of a black body, he did not think it would be possible to keep the temperature sufficiently constant to enable it to be used as a standard.

A paper on "*Inductance and Resistance in Telephone and other Circuits*" was read by Dr. J. W. NICHOLSON.

A general formula for the effective inductance of a circuit consisting of two long parallel wires has been given by the author, and is suitable for cases in which the current distribution in either wire is greatly affected by the frequency of alternation. In the present paper certain important cases are examined in detail, and formulæ are obtained capable of immediate use. A calculation of the effective resistance is also made in each case. Attention has been mainly directed to that of the simple telephone circuit, in which the leads are not twisted round each other in order to annul the inductive effects of the earth and of neighbouring circuits. Throughout the investigation only iron and copper-wires as the two extreme cases are considered. The large permeability of iron completely changes the character of the effect of frequency on its self-induction, as compared with other metals. To all metals greatly used in practice, except iron, the formulæ developed for copper-wires may be applied with a nearly identical order of accuracy.

A "*Note on Terrestrial Magnetism*" by Mr. G. W. WALKER, and a paper by Mr. A. EAGLE, "*On the Form of the Pulses constituting full Radiation or White Light*," were taken as read.

SOCIETY OF CHEMICAL INDUSTRY.

(LONDON SECTION).

Ordinary Meeting, June 7th, 1909.

Dr. J. LEWKOWITSCH in the Chair.

"*Industrial Fellowships*." By Prof. R. KENNEDY DUNCAN.

The following is an example of the conditions attaching to the system of Industrial Fellowships of the University of Kansas. Six such Fellowships have so far been accepted by the University of Kansas:—

Fellowship No. 7.

For the purpose of promoting the increase of useful knowledge, the University of Kansas accepts from the A.B.C. Glass Company, having head offices at New York, the foundation of a temporary Industrial Fellowship to be known as the A.B.C. Fellowship.

The exclusive purpose of this Fellowship is an investigation into the optical properties of glass in relation to its chemical constitution, to the furtherance of which the holder shall give his whole time and attention, with the exception of three hours a week which he shall give to work of instruction in the chemical department.

The Fellow shall be appointed by the Chancellor of the University, the Director of the Chemical Department, and the Professor of Industrial Chemistry; he shall have made previously a reputation in research; he shall be a Member of the University, and shall pay all regular fees with the exception of fees for laboratory and supplies, for which his instruction shall be taken in lieu, unless in the opinion of the appointers his demands become excessive, in which case the donor shall be expected to reimburse the University; he shall work under the advice and direction of the Professor of Industrial Chemistry; and he shall forward, periodically, through the Professor of Industrial Chemistry, reports of the progress of his work to the A.B.C. Company.

For the support of this Fellowship, which shall extend through a period of two years from the date of appointment of the Fellow, the A.B.C. Glass Company agrees to pay 1500 dols. per year, payable annually to the University

on the date on which the Fellow begins work at the University. This sum shall be paid by the University in monthly instalments to the holder of the Fellowship.

Any and all discoveries made by the Fellow during the tenure of this Fellowship shall become the property of the A.B.C. Glass Company, subject, however, to the payment by them to the Fellow of 10 per cent of the net profits, to be commuted at the desire of either party through the arbitration provided for herein, arising from such discoveries, it being understood that the Fellow shall be regarded as the inventor. At any time during the tenure of his Fellowship the holder shall, at the option of the donor, take out patents at the expense of the donor on condition that at the time of making application therefor he shall assign his right to the donor under the conditions of this agreement. At or before the expiration of the Fellowship, the business services of the Fellow may be secured by the A.B.C. Glass Company for a term of three years on condition that the terms of such services are satisfactory to both parties at interest.

In the event of any disagreement between the donor and the holder of this Fellowship, it is understood and agreed that the Chancellor of the University, or one whom he may appoint, shall act as arbiter as to all matters of fact, that his decisions shall be binding upon the parties at issue, and that they shall obtain such decision before having recourse to the Courts.

It is also understood and agreed that during the tenure of this Fellowship the holder may publish such results of his investigation as do not, in the opinion of the Company, injure its interests, and that on the expiration of the Fellowship the holder thereof shall have completed a comprehensive monograph on the subject of his research, containing both what he and others have been able to discover. A copy of the monograph shall be forwarded to the A.B.C. Company, and a copy shall be signed and placed in the archives of the University until the expiration of three years from that date, when the University shall be at liberty to publish it for the use and benefit of the people.

"The Colorimetric Determination of Lead in the presence of Iron, with some Notes on the Preparation of Lead Free Reagents." By J. M. WILKIE.

The author shows that the methods at present in use for the colorimetric determination of lead as sulphide are highly inaccurate in the presence of minute traces of iron.

The precipitation of lead by ferric hydroxide was found in certain cases to be complete if the ratio of iron to lead exceeded two. This property of ferric hydroxide is of great value in the preparation of lead free reagents.

These sources of error are eliminated, and the addition of tartaric acid becomes quite superfluous if the precaution is taken to reduce ferric iron, and to ensure that precipitation of ferrous hydroxide takes place within the sphere of action of the potassium cyanide. The mode of working adopted is to reduce with sodium sulphite or thiosulphate in acid solution, to add potassium cyanide directly to the acid solution of the ferrous salt, and then excess of ammonia, and heat gently until colourless.

For quantitative conversion to ferrocyanide not less than three to four times the theoretical amount of cyanide can be conveniently used. Sodium thiosulphate has no special features as a reducing agent in work of this kind.

Constitution of the Salts of the Phthaleins, and the cause of Colour in the Triphenylmethane Series." By A. G. GREEN.

Whilst strong evidence has been adduced by Green and King in favour of the quinonoid structure of the coloured salts and ethers of the phthaleins, there still remain a few facts which are not fully explained. One of these is the remarkable difference in colour between the quinonoid diethyl ethers and the corresponding alkali salts (orange in the first case and violet-red in the second), whilst another is the circumstance that the substitution of one only of the phenolic hydroxylic groups by methoxyl, in either phenol-

phthalein or in quinolphthalein, suffices entirely to prevent the formation of coloured salts with alkalis.

By an extension of Von Baeyer's theory of oscillatory quinonoid bonds, but employing the usual Fittig formula of quinonoid compounds instead of the Graebe formula used by Von Baeyer, and by the assumption that the movement of the metallic or acid ion between the two salt-forming groups is the determining cause of the quinonoid oscillation, a satisfactory explanation can be given of the above and other facts. Thus the effect of salt-formation on colour intensity, the function of auxochromic groups, and the increase of basicity according to the "power law" are readily explained.

NOTICES OF BOOKS.

Introduction to the Chemistry and Physics of Building Materials. By ALAN E. MUNBY. London: Archibald Constable and Co., Ltd. 1909.

IN the first part of this book a courageous and, on the whole, successful attempt is made to explain in comparatively few words the fundamental principles of chemistry, physics, and geology upon which is based the use of modern building materials. Although the author had in his mind the requirements of those who know no natural science whatever, and wrote specially for them, the summary will perhaps be of more value for the practical men who have forgotten the little they have learnt, or who fail to see the direct application of principles with which they are already familiar. The section on chemistry is perhaps a little too ambitious; a knowledge of the atomic theory and of the use of formulæ and equations is hardly necessary, judging from the style of the main portion of the book. The characteristics of the common minerals and the examination and testing of stones are treated with sufficient completeness to be of use to the practical man, and cements and plasters are given full consideration, Michaeli's colloidal theory of the setting of cements being discussed at some length. The metals are treated in the same way as the minerals, and a chapter on timber gives a short account of its properties, the causes of and remedies for its decay. The chapters on paints which conclude the book are somewhat superficial, general information only being given upon the use of paints as preservatives and the general characters of their constituents.

The Manufacture of Paper. By R. W. SINDALL, F.C.S. London: Archibald Constable and Co., Ltd. 1908.

THE difficulty of making an account of the manufacture of paper represent correctly present-day methods, at the same time avoiding technicalities which are beyond the understanding of the general public, has been very successfully surmounted in this book. The historical notice with which it begins is interesting enough to arrest the attention of the reader, who will pass on to the chapters on the manufacturing process with a clear idea of the development of modern from the original primitive methods. Certain parts of the book, such as the chapter on cellulose and paper-making fibres, are perhaps a trifle intricate, but they can satisfactorily be used for reference if they are not read consecutively. The deterioration of paper, which is a topic which has occupied much attention in recent times, is treated in the last chapter, in which some notes are also given upon the testing of the physical properties of paper, and the standard to which good papers of various classes should attain.

Modern Organic Chemistry. By CHARLES ALEXANDER KEANE, D.Sc., Ph.D., F.I.C. London and Felling-on-Tyne; The Walter Scott Publishing Co., Ltd. 1909.

THE great aim of this book is to make the vast fields of knowledge of organic chemistry accessible to the general

reader whose scientific training has not included this subject, or to the specialist in some other branch of science. Hence a general view is given of the whole subject, with a clear statement of the problems and methods which are characteristic of it, and any points of special difficulty, such as the interpretation of structural formulæ, are treated at length. The book will also be of great value to the student to supplement his reading in text-books and original papers. He will find that it puts before him a clear picture of the principles of organic chemistry, omitting details and emphasising generalisations, and the references to papers describing classical investigations and discoveries of great importance have been well chosen. The book is utterly unlike the usual type of text-book, and it would be an interesting experiment, which might possibly be attended by a considerable measure of success, to put it into the hands of a beginner.

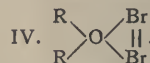
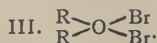
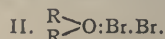
The Chemistry and Literature of Beryllium. By CHARLES LATHROP PARSONS, B.S. Easton, Pa.: The Chemical Publishing Co. London: Williams and Norgate. 1909.

It would be a good thing for the furtherance of chemical research if each one of the rarer elements were summarised after the fashion of this book. The difficulties of finding out exactly what work remains to be done on an element are often considerable, and even the thorough searching of periodical literature often brings to light only contradictory statements upon which further confirmatory work has to be done before any real advance is made. In the case of beryllium this monograph entirely does away with the laborious task of collecting information from scattered sources, for the author has prepared an exhaustive study of the history and chemistry of the element, and of its normal, basic, and double salts. In addition an excellent bibliography is included; besides the titles of all original articles on beryllium, and the names of the papers in which they were published, important abstracts are also enumerated, while a very short criticism of the results reported in each paper is added.

results, the propenyl derivative remaining unchanged. Hence the latter can be separated since it is soluble in ether and volatile in a current of steam, while the acetomeric compound of the allyl derivative is practically insoluble in ether and is not driven over by steam. With zinc and caustic soda the aceto-compound yields the free allyl derivative.

Peroxides.—S. Tanatar.—Some years ago the author showed that nickel peroxide yields small quantities of hydrogen peroxide with sulphuric acid. Larger quantities of H_2O_2 can be prepared by making a salt from nickel peroxide if the formation of the salt develops sufficient heat. For instance, the action of hydrocyanic acid in presence of potassium cyanide on nickel peroxide gives the double salt K_2NiCy_4 , and the solution contains much more H_2O_2 than that obtained by dissolving the peroxide in sulphuric acid. With silver, cobalt, and lead peroxides apparently no H_2O_2 is formed. The author thinks that Pellini and Meneghini's "true nickel peroxide," which gave no hydrogen peroxide with sulphuric acid, was a molecular compound of nickel peroxide with hydrogen peroxide, analogous to the molecular compounds which H_2O_2 forms with many organic and inorganic compounds.

Ether-Oxonium Dibromide.—W. Tschelinzeff and W. Kepowaloff.—When ether is energetically shaken with bromine an oil of composition $[(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{Br}_2]_2$ is obtained. This substance behaves like a true compound towards different organic solvents. It acts energetically on many metals, zinc, magnesium, iron, nickel, and cobalt, while it has only a very feeble action on the alkalis. It appears to react with aqueous ammonia solution and a heavy oily liquid is formed, but this product has not been obtained in the pure state. With the oxides of heavy metals the dibromide yields peroxide, $\text{C}_2\text{H}_5 > \text{O} < \text{Br} \rightarrow \text{C}_2\text{H}_5 > \text{O} : \text{O}$. Magnesium organo-compounds react as follows:— $\text{C}_2\text{H}_5 > \text{O} < \text{Br} + \text{Mg} \cdot \text{C}_2\text{H}_5 = \text{C}_2\text{H}_5 > \text{O} + 2\text{MgBrI} + \text{C}_4\text{H}_{10}$. Of the four possible formulæ of the oxonium dibromides, those of types III. and IV. are most probable and satisfactorily express the behaviour of the substances.



CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft,
Vol. xlii., No. 7, May 8, 1909.

Rhodium.—A. Gutbier and M. Riess.—The authors have confirmed the fact that hydrazine sulphate reduces rhodium compounds to the metal, and if solutions which are not too concentrated are used the method can be employed for the quantitative determination of rhodium.

Action of Antimony Hydride on Dilute Silver Solution.—Hans Reckleben.—The investigation of the action of antimony hydride on silver solutions shows that it is erroneous to suppose that antimony and arsenic behave differently in this respect. In both cases the reaction is the same, a mixture of much hydroxide and a little metal (arsenic or antimony) being formed and silver precipitated. The only difference is that the difficultly soluble H_3SbO_3 remains in the precipitate while the easily soluble H_3AsO_3 goes into the solution. The reaction takes place in two stages, represented by the following equations:— $\text{H}_3\text{Sb} + 3\text{AgNO}_3 = \text{Ag}_3\text{Sb} + 3\text{HNO}_3$, $\text{Ag}_3\text{Sb} + 3\text{AgNO}_3 + 3\text{H}_2\text{O} = 6\text{Ag} + \text{H}_3\text{SbO}_3 + 6\text{HNO}_3$.

Separation of Allyl and Propenyl Compounds in Etheral Oils.—L. Balbiano.—When mercuric acetate solution acts on a mixture of propenyl and allyl compounds, only the acetomeric compound of the allyl derivative

MISCELLANEOUS.

Royal Society of Arts Albert Medal.—The Council of the Royal Society of Arts, with the approval of His Royal Highness the Prince of Wales, President of the Society, have awarded the Albert Medal of the Society for the current year to Sir Andrew Noble, K.C.B., D.Sc., D.C.L., F.R.S., "in recognition of his long-continued and valuable researches into the nature and action of explosives, which have resulted in the great development and improvement of modern ordnance."

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Caloric Values.—Would any reader kindly advise me if there are any books published containing an extensive and up-to-date list of caloric values or heats of combustion of the inorganic elements and compounds, together with the titles and publishers of such books.—GORDON MILLS.

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